



# The effect of firing temperatures on phase formation, microstructure and dielectric properties of $\text{Bi}_{0.5}(\text{Na}_{0.74}\text{K}_{0.16}\text{Li}_{0.10})_{0.5}\text{TiO}_3$ ceramics synthesized via the combustion route

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## Abstract

A novel combustion technique has been developed to prepare  $\text{Bi}_{0.5}(\text{Na}_{0.74}\text{K}_{0.16}\text{Li}_{0.10})_{0.5}$  (abbreviated as BNKLT1610) ceramics.  $\text{CH}_4\text{N}_2\text{O}$  was used as a fuel to reduce the reaction temperature. The effects of calcination temperature and sintering temperature on the phase and morphology evolution of the perovskite samples were investigated. The vaporization of raw materials and products caused the formation of a secondary in calcined powders and sintered ceramics, respectively. The XRD patterns suggested the BNKLT1610 ceramics show the coexistence of rhombohedral and tetragonal phases, and the relative amount of each phase correlates with the sintering temperature. The dielectric peak at depolarization temperature ( $T_d$ ) was exhibited in all samples while the dielectric peak at maximum dielectric temperature ( $T_m$ ) was observed only in the samples sintered at high temperatures. The dielectric results persuade core–shell structure is formed in prepared samples. Increasing sintering temperature caused the grain core to enlarge and the grain shell to become thinner. The dielectric constants are highly affected by secondary phase formation and densification. The highest value  $\epsilon_r$  of 1210 was obtained from the sample sintered at 1000 °C, which is significantly higher than BNKLT1610 prepared via the solid-state reaction method.

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**Keywords:** C. Dielectric properties; BNT; Combustion technique; Core–shell structure

## 1. Introduction

Lead-free piezoelectric ceramics have attracted increasing attention because the PbO in lead-based piezoelectric ceramics is volatile and detrimental to human health and the environment. Bismuth sodium titanate ( $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ , BNT), discovered by Smolenskii et al. in 1961 [1], is one of the most important lead-free piezoelectric materials. This ceramic shows strong ferroelectricity of  $P_r = 38 \mu\text{C}/\text{cm}^2$  and high Curie point of  $T_C = 540 \text{ °C}$  [1].

However, because of its high coercive field ( $E_c = 73 \text{ kV}/\text{mm}$ ) and relatively large conductivity, pure BNT is difficult to be poled and is limited in its typical applications [2]. This is because both Bi and Na at the A-site of  $\text{ABO}_3$  perovskite tend to evaporate during sintering at high temperature. Therefore, A-site vacancies should be easily formed in BNT ceramics and effect the conductivity of the materials [3].

Many researchers have attempted to improve BNT-properties by selecting some cation substituted on the A-site of a BNT system [4–10]. Yang et al. [5] studied the effects of K substituted to Na at the A-site of BNT perovskite in a range of 10–20 mol% on crystal structure, microstructure and electrical properties. The results indicated 18 mol% of K substitution induced an occurrence in the MPB region between the rhombohedral–tetragonal

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phases, which enhanced the dielectric properties of the ceramics. Lin et al. [10] demonstrated that a small amount of Li could decrease sintering temperature and improve the densification of BNT–BT ceramics. The study on Li and K substituted BNT was extensively investigated by Lu et al. [4]. The XRD results indicated that the  $\text{Bi}_{0.5}(\text{Na}_{0.74}\text{K}_{0.16}\text{Li}_{0.10})_{0.5}\text{TiO}_3$  or BNKL1610 composition showed the coexistence of a rhombohedral and tetragonal structure which suggests this composition is located near the MPB region. Moreover, the substitution of Li and K for BNKL1610 greatly improved the electrical properties of BNT such as increasing  $d_{33}$  from 78 to 160 pC/N, increasing  $k_p$  from 0.16 to 0.35 and increasing  $\epsilon_r$  from 420 to 1080.

In terms of the preparation process, BNT-based ceramics were fabricated via the solid-state reaction method [11,12]. The raw materials were heat treated at 800–900 °C for 2–5 h in a calcination process and at 1050–1200 °C for 2–5 h in a sintering process. The secondary phases were formed due to the vaporization of raw materials at high temperature in the preparation processes [11]. To avoid this problem, BNT and BNT-based ceramics have been prepared by several wet chemical methods such as the sol–gel route [13], the hydrothermal method [14] and the molten salt synthesis [15]. However, it is well known that these chemical methods require a long processing time, special equipment and have a complex procedure [16].

Recently, the combustion technique has become an attractive technique to prepare ferroelectric materials because it is uncomplicated [16–19]. Moreover, the released energy from fuel decomposition helps to reduce the firing temperatures in the preparation process. Therefore, the purpose of this study was to synthesize BNKLT1610 ceramics via the combustion route. The effect of firing temperatures on phase formation, microstructure and dielectric properties of BNKLT1610 ceramics was also investigated.

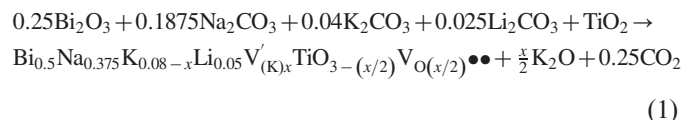
## 2. Experimental procedure

The starting chemicals for producing  $\text{Bi}_{0.5}(\text{Na}_{0.74}\text{K}_{0.16}\text{Li}_{0.10})_{0.5}\text{TiO}_3$  (BNKLT1610) ceramics were reagent grade bismuth oxide ( $\text{Bi}_2\text{O}_3$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ), lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) and titanium oxide ( $\text{TiO}_2$ ). The raw materials were weighed and mixed by ball milling in ethanol for 24 h. After the raw materials were dried and ground into fine powders, they were mixed with urea ( $\text{CH}_4\text{N}_2\text{O}$ ) in a ratio of 1:2 in an agate mortar. The starting materials were calcined at various calcination temperatures ranging from 600 to 900 °C for 2 h. The X-ray diffraction (XRD) was employed to identify the phase formation and the optimum firing temperature for the prepared powders. Calcined powders obtained from appropriate condition were selected to press into pellets of 15 mm in diameter using uniaxial pressing in a stainless steel mold. The pellets were subsequently sintered between 950 and 1150 °C with a dwell time of 2 h. The phase formation behavior of the sintered ceramics was characterized by the X-ray diffraction pattern. The microstructure of the calcined powders was studied using transmission electron microscopy (TEM). SEM photographs

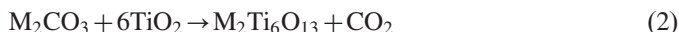
were used to observe morphology and measure average particle size and grain size of the calcined powders and sintered ceramics. The bulk densities of the sintered samples were measured by the Archimedes method using distilled water as medium. Silver electrodes were applied on the opposite disk faces and were heated at 500 °C for 5 min. Dielectric measurement was carried out using a LCR meter connected to a PC.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the BNKLT1610 powders calcined at different temperatures from 600 to 900 °C. At a low calcination temperature (600 °C), the diffraction peaks can be indexed as the rhombohedral perovskite phase for BNKLT1610. This corresponded to the thermal analyzed by the literature [14], which indicated that the BNT perovskite crystal can be formed above 500 °C. However, a small amount of the secondary phase of  $\text{M}_2\text{Ti}_6\text{O}_{13}$  as described by Naderer et al. [11] was detected. The formation of the secondary phase was caused by the volatilization of  $\text{K}_2\text{O}$  with high lead vacancies concentration as shown in the following equation:



The evaporation of  $\text{K}_2\text{O}$  caused a shift in the A/B ratio of cation in composition. To reduce the number of vacancies and reduce the deviation of the A/B ratio, the secondary phase of  $\text{M}_2\text{Ti}_6\text{O}_{13}$  was formed from starting materials as shown in Eq. (2) where M refers to Na and/or Li and/or K [11].



By increasing the calcination temperature, the secondary phase was decreased and completely eliminated when the calcination temperature reached 750 °C. The calcining condition of 750 °C for 2 h, which produced the pure BNKLT1610

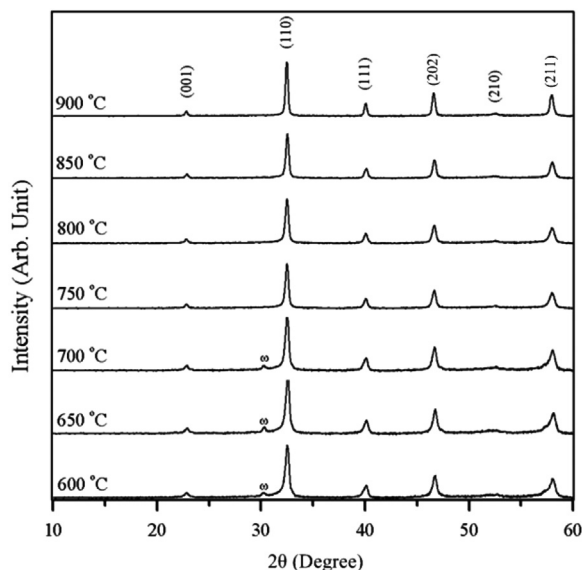


Fig. 1. XRD patterns of BNKLT1610 powders calcined at different temperatures: ( $\omega$ )  $(\text{K, Na, Li})_2\text{Ti}_6\text{O}_{13}$ .

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