Influence of SFT Content on Physical, Mechanical and Dielectric Properties of BNKT-SFT Binary Ceramic System

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Abstract. In this research, the binary solid solution \( \text{Bi}_{0.5}(\text{Na}_{0.8\,\text{K}_{0.16}})_{0.5}\text{TiO}_3 \) and \( \text{Sr}(\text{Fe}_{0.5}\text{Ta}_{0.5})\text{O}_3 \) in the system of \((1-x)\text{BNKT-xSFT}\) was synthesized by solid-state reaction technique. The mixed powder and ceramics of \((1-x)\text{BNKT-xSFT}\) were calcined at 900 °C for 2 h and sintered at 1125 °C for 2 h. The sintered ceramic samples were investigated phase formation, densification, mechanical properties, and dielectric constant at room temperature. The XRD analysis of all condition samples shows a pure phase perovskite structure. The maximum of bulk density, HV, HK microhardness, the elastic modulus, fracture toughness, and dielectric constant were found at \( x = 0.04 \) condition which the value is 5.877 g/cm\(^3\), 6.21 GPa, 5.39 GPa, 181.12 GPa, 0.19 MPa-m\(^{1/2}\) and 1.404, respectively. A small among SFT content shows an improvement of densification, mechanical properties, and dielectric constant in \((1-x)\text{BNKT-xSFT}\) ceramics. The relations of these results were discussed and compared to the previously reported.

1. Introduction

Nowadays, the environmental protection is more important and concern due to the environmental impact have effect with all living things. Therefore, lead-free materials are very attractive for many research which the aim of use it replace lead-based material. That is well know the process of fabrication of lead-based material produce a hazard compound and high toxic such as lead oxide (PbO) [1-2]. Bismuth sodium potassium titane (BNKT) ceramics system is a lead-free perovskite ceramic which is interested by many focussing on lead-free electro-ceramics developers. Because, they have many interesting properties e.g., phase transition, dielectric, ferroelectrics and electric field induce strain properties at morphotropic phase boundary (MPB) that the combined phase of tetragonal and rhombohedral phase. The MPB of BNKT ceramics system was located at 16-20 mol% of BKT in BNKT ceramics. The highest values of \( d_{33} \) is 157 pC/N at 20 mol% of BKT [3]. Moreover, BNKT ceramics system can improved properties by various method. The synthesis by solid-solution method is more effective for improve properties of electro-ceramics. Recently, Ullah et al.[4] was reported that the solid-solution of \((1-x)\text{Bi}_{0.5}(\text{Na}_{0.8}\text{K}_{0.20})_{0.5}\text{TiO}_3\)\(-x(\text{Ba}_{0.7}\text{Sr}_{0.3})\text{TiO}_3\); \((1-x)\text{BNKT-xBST}\) show good properties including tan\(\delta \) (0.03), \( k_p \) (38%), \( Q_m \) (120), and \( d_{33} \) (223 pC/N) at the composition of \( x = 0.03 \). As well as, many reported show a high electric field induced strain e.g. \( S_{\text{max}}/E_{\text{max}} \) of 930 pm/V with 0.94Bi\(_{0.5}\)(Na\(_{0.75}\)K\(_{0.25}\))\(_{0.5}\)TiO\(_3\) - 0.06BiAlO\(_3\) by Lee et al. [5], \( S_{\text{max}}/E_{\text{max}} \) of 649 pm/V with 0.95Bi\(_{0.5}\)(Na\(_{0.8}\)K\(_{0.20}\))\(_{0.5}\)TiO\(_3\) - 0.05Ba(Ti\(_{0.90}\)Sn\(_{0.10}\))O\(_3\) by Jaita et al. [6], and \( S_{\text{max}}/E_{\text{max}} \) of 636 pm/V with
The mechanical and physical properties of electroceramics are significant for determining electrical properties and suggest a type of application. In the current reports, the mechanical properties of BNKT-based materials were scarce. Recently, there was a report that both the mechanical and electric properties of BNKT-based can be improved by modifying with BaTi$_{0.99}$Nb$_{0.01}$O$_{3}$; BTNb solid solution as it is mentioned in Manotham et al. [9]. Therefore, this has motivated us to synthesize and characterize the properties of (1-x)Bi$_{0.5}$(Na$_{0.8}$K$_{0.2}$)$_{0.5}$TiO$_{3}$-xSr(Fe$_{0.5}$Ta$_{0.5}$)O$_{3}$; (1-x)BNKT-xSFT where x=0.00-0.04. The physical, mechanical, and dielectric properties were studied and discussed with previous works.

2. Material and Methods

2.1. Preparation of sample

The solid solution of (1-x)Bi$_{0.5}$(Na$_{0.8}$K$_{0.2}$)$_{0.5}$TiO$_{3}$-xSr(Fe$_{0.5}$Ta$_{0.5}$)O$_{3}$; (1-x)BNKT-xSFT, x varies from 0.00-0.04, were fabricated via solid-state reaction technique. High purity metal oxides of Bi$_2$O$_3$, Na$_2$CO$_3$, K$_2$CO$_3$, TiO$_2$, SrCO$_3$, Fe$_2$O$_3$, and Ta$_2$O$_5$ were used for raw materials. All raw materials were weighted and stoichiometrically for each condition. Then, each condition was mixed via the conventional ball milling method for 24 h. Those mixed powders were calcined at 900 °C for 2 h. The obtained powders were sieved and pressed for a pellet shape. The green pellet of all conditions was sintered at 1125 °C for 2 h.

2.2. Characterization of samples

The ceramics of (1-x)BNKT-xSFT have studied bulk density, phase formation, mechanical, and dielectric properties at room temperature. The bulk density was determined using Archimedes’ method. The phase formation of ceramics samples was characterized via X-ray diffraction method. For characterization of mechanical properties, the samples were well polished by diamond compound for shiny smooth surface. The obtained polished samples were measured mechanical properties by micro hardness tester. For the dielectric measurements, the samples were polished both side and coated silver compound for use as an electrode. The well preparing electrode samples were measured dielectric constant at room temperature via high precision LCR meter (4284A model).

3. Results and Discussion

The phase formation of ceramics was characterized via X-ray diffraction technique. The XRD spectra of the (1-x)BNKT-xSFT are shown in Figure 1. The XRD spectra pattern of all ceramics conditions shows the clear single perovskite phase without an obvious secondary phase following characteristic with JCPDS number of 0-036-0340, 0-036-0339, and 1-074-2476 which are BNT, BKT, and SFT, respectively. There is no evidence of impurity phase such as the phase of Bi$_4$Ti$_3$O$_{12}$ which was found in previous work [10]. It can be noted that the (1-x)BNKT-xSFT where x=0.00-0.04 is stable perovskite structure and easy to fabricate by solid solution technique which added a few amounts of SFT. Figure 2 shows the bulk density of the (1-x)BNKT-xSFT ceramics. The trend of bulk density of these ceramics slightly increases with increasing the content of SFT. The value of bulk density is in the range of 5.810-5.877 g/cm$^3$ which maximum at x=0.04. The increased density of this ceramics system may due to the decrease in porosity in ceramics and the mixed property of the density of the constituent compound. The theoretical density of BNT, BKT, and SFT are 5.99, 5.93, and 6.72 g/cm$^3$, respectively. The increase of density may cause by the increased SFT content.
Figure 1. X-ray diffraction of the (1-x)BNKT-xSFT ceramics where x=0.00-0.04.

Figure 2. Bulk density of the (1-x)BNKT-xSFT ceramics where x=0.00-0.04.
The mechanical properties are determined by micro hardness (both of Vickers micro hardness (HV) and Knoop micro hardness (HK)), the elastic modulus (E), and fracture toughness (K\text{IC}). The summary of mechanic properties and dielectric at 1kHz room temperature show in table 1. The HV and HK were performed by empirical formula which show in equation (1) and (2) [11-12]. Each parameter in formula was collected from the indenter print by an optical microscope. The appearance of the indenter print of HV and HK show in Figure 3 (a) and (b), respectively.

\[
HV = \frac{(1.854)P}{d^2}
\]

\[
HK = \frac{(14.23)P}{d^2}
\]

where, P= load (N) in this work used 10 N and d= half-length of long diagonal (µm). The value of both micro hardness slightly increase with increasing among of SFT content in the (1-x)BNKT-xSFT ceramics. The highest value micro hardness is 6.21 GPa for HV and 5.39 GPa for HK at x=0.04. This resulted similar found by Manotham et al.[9] and Kruea-In et al.[13] which adding small amount of BTNb and Bi_{0.5}(Zn_{0.5}Zr_{0.5})O₃; BZZ in BNKT-based [13]. Moreover, the elastic modulus and fracture toughness were investigated as shown in table 1. The trend of E and K\text{IC} had a same direction of micro hardness. The increase of mechanical properties may be due to affected of density increasing and reduce porosity by SFT in (1-x)BNKT-xSFT ceramics. It can be noted that mechanical properties of the BNKT-based ceramic can be improved by the added SFT.

| Composition | HV(GPa) | HK(GPa) | E(GPa) | K_{IC} (MPa m^{1/2}) | \varepsilon_r @ 10 kHz |
|-------------|---------|---------|--------|----------------------|------------------------|
| 0.00        | 5.78    | 5.09    | 143.82 | 0.17                 | 1,082                   |
| 0.01        | 5.81    | 5.11    | 149.61 | 0.18                 | 1,111                   |
| 0.02        | 5.98    | 5.33    | 151.13 | 0.18                 | 1,172                   |
| 0.03        | 6.01    | 5.35    | 157.59 | 0.19                 | 1,376                   |
| 0.04        | 6.21    | 5.39    | 181.12 | 0.19                 | 1,404                   |
Figure 3. the indenter prints of (a) HV and (b) HK of x=0.01.

Frequency dependent of the dielectric constant ($\varepsilon_r$) of (1-x)BNKT-xSFT ceramics measured over a frequency rang 10 kHz-2MHz at room temperature are shown in Figure 4. The dielectric constant of all ceramic samples exhibited decreasing with measuring higher frequencies may be cause by the active presence of all types of polarization in dielectric materials as mention in Moulson and Herbert [14]. The various types of polarization i.e. space charge, dipolar, ionic and atomic polarization affect to the dielectric constant value. The observation of the higher values of dielectric constant at low frequencies than a dielectric constant at high frequencies measurement may due to the active of all types of polarization. At low frequencies measurement, all of types of polarization are active but at high frequencies some of types of polarization are active. The dielectric constant at a frequency of 10 kHz is also listed in Table 1. The dielectric constant increased from 1,082 to 1,404 with the maximum at x=0.04 corresponding to the increasing among of added SFT. The increasing of a dielectric constant of this resulted may mainly connect to the densification of ceramics.
Figure 4. Frequency dependent of the dielectric constant of (1-x)BNKT-xSFT ceramics.

4. Conclusion
Effect of SFT on the physical, mechanic and dielectric properties at room temperature were studied. All sintered ceramics samples exhibited the single perovskite phase. The densification, mechanic and dielectric constant at room temperature are improved by added of SFT in (1-x)BNKT-xSFT ceramics. The x=0.04 sample showed an improvement of bulk density (5.877 g/cm$^3$) mechanical properties (HV=6.21 GPa, HK=5.39 GPa, E=181.12 GPa and K$_{ic}$ = 0.19 MPa-m$^{1/2}$) and dielectric constant at 10 kHz room temperature (1,404).

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