Synthesis and Characterization of BNKT Co-Added Nb and Li Lead-free Composite Ceramics

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Abstract

The effects of co-added Nb and Li additive on phase behavior, densification, microstructure and mechanical properties of $Bi_{0.5}(Na_{0.81}K_{0.19})_{0.5}TiO_3$composite ceramics were investigated. The samples were synthesized by solid state reaction technique, where powders were calcined at 850 °C for 4 h and ceramics were sintered at 900-1050 °C for 2 h. Phase formation was determined by X-ray diffraction technique (XRD). The X-ray diffraction analysis of the ceramics suggests that all samples exhibited a perovskite structure at low concentration Nb and Li additive. The physical and mechanical properties behaviors slightly changed with increasing the additive contents.

Keywords: Phase formation, Microstructure, Mechanical Properties

1. Introduction

The ferroelectric and piezoelectric materials are attractive and have a prominent status because of it play important roles in electromechanical such as dielectric resonators, actuators, hydrophones,pressure sensors and etc. The Pb-based materials such as lead zirconium titanate (PZT) has been used predominantly over the last few decades (Zhang et al, 2007). It is well known the vapor of lead during fabricated route has highly toxic. Forconcern this problem, the lead free electro-ceramics have been many investigated such as bismuth sodium titanate based ($(Bi_{0.5}Na_{0.5})TiO_3$, BNT-based)(Hiruma et al, 2008), barium titanate based ($BaTiO_3$, BT-based)(Kruea-In et al, 2012), and potassium sodium niobate based ($(K_{0.5}Na_{0.5})NbO_3$, KNN-based)(Hayati et al, 2010). Among these materials, the BNT is an interesting lead free piezoelectric material which is a perovskite structure anda rhombohedral symmetry. This material has Bi^{3+}, Na^{+} on A-site and Ti^{4+} on B-site of the ABO_3perovskite structure. BNT has been considered to be a promising candidate as a lead-free ferroelectric material to replace the widely used lead based materials due to its good both of ferroelectric and piezoelectric propertiesat room temperature. However, the large coercive field of BNT ceramics makes them difficult for a poling.To solve this problem, many BNT-based solid solutions have been fabricated to produce improved properties. Among these modified BNT-based, the (1-y)BNT-yBKT (BNKT) ceramics have been intensively investigatedby many authors(Sasaki et al, 1999:Kumer et al, 2012). Because they have excellent ferroelectric and piezoelectric properties at close to morphotropic phase boundary (MPB) which is changed between rhombohedralphaseand tetragonal phase. The MPB of BNKT ceramics is around$0.16 < y < 0.20$ (Ullah et al, 2010). Recently, many research groups have reported that the adding small among of metal oxide on BNKT ceramics at MPB could be improved dielectric and ferroelectric properties of this

material (Pham et al, 2010).However, the physical and mechanical properties of ceramics are significant determination of electrical properties and application condition. In this study, we have investigated the effects of small additions of Nb_2O_5-Li_2CO_3in a composites of $Bi_{0.5}(Na_{0.81}K_{0.19})_{0.5}TiO_3$-x($Nb_2O_5$-$Li_2CO_3$) in term of phase formation, densification, microstructural and mechanical properties.

2. Research Objectives

The objectives of this research were as follow:

2.1 Synthesis and characterization of $Bi_{0.5}(Na_{0.81}K_{0.19})_{0.5}TiO_3$co-added Nb and Li composite ceramics.

2.2 To study the influences of Nb and Li on the phase formation, densification, microstructure and mechanical properties of this composite ceramics.

3. Research Methodology

The conventional solid state reaction technique was used to fabricate the powders of $Bi_{0.5}(Na_{0.81}K_{0.19})_{0.5}TiO_3$. The high purity grade metal oxide powders of Bi_2O_3, Na_2CO_3, K_2CO_3 and TiO_2 were used as starting materials. All powders were weighted following the stoichiometry chemical formula. The weighted powders were mixed by a planetary ball milled withethanol and partially stabilized zirconia as the medium for 24 h. The slurry after mixed was dried and sieved. The obtained powders were calcined at 850 °C for 4 h in a covered alumina crucible. The high purity perovskite phase obtain using powers at the optimum calcination temperatures were then added with Nb_2O_5 and Li_2CO_3. The $Bi_{0.5}(Na_{0.81}K_{0.19})_{0.5}TiO_3$-x($Nb_2O_5$-$Li_2CO_3$) with x=0, 3, 6 and 9 wt.% were weighted and then mixed. After drying, the obtained powders were added by 3 wt.% of a polyvinyl alcohol binder. The resulting powders were the cold isostatically pressed into pellets of 10 mm in diameter. The green pellets were sintered at 900-1050 °C for 2 h in order tooptimizesintering temperature for each composition.Phase formation was determined using the X-ray diffraction technique (XRD). The densities of the samples were determined using the Archimedes method with distilled water as the fluid media. Morphology of ceramics was studied by a scanning electron microscope (SEM). The mechanical properties of the ceramics were determined by a Vickers hardness tester, Young's modulus, and fracture toughness.

4. Research Results

The results were presented according to the research objectives as follows:

4.1 Phase formation

Figure 1 shows the XRD pattern of all composite ceramics which 2θ were 20°-60°. These data showed that a single perovskite phase was found at x=0 and 3 wt.%. For x=3 wt.%, it indicated that Nb_2O_5 and Li_2CO_3 diffused in to $Bi_{0.5}(Na_{0.81}K_{0.19})_{0.5}TiO_3$ lattice during sintering. However, the apparent trace of secondary phase can be observed at x= 6 and 9 wt.%. Both samples were analyzed by comparison of peak location the standard ICDD reference pattern spectra for determining secondary phase. The secondary phase or

impurity phase at 28.03°, 29.97°and 43.56°were BiO_2, $Bi_4Ti_3O_{12}$and unknown phase, respectively.

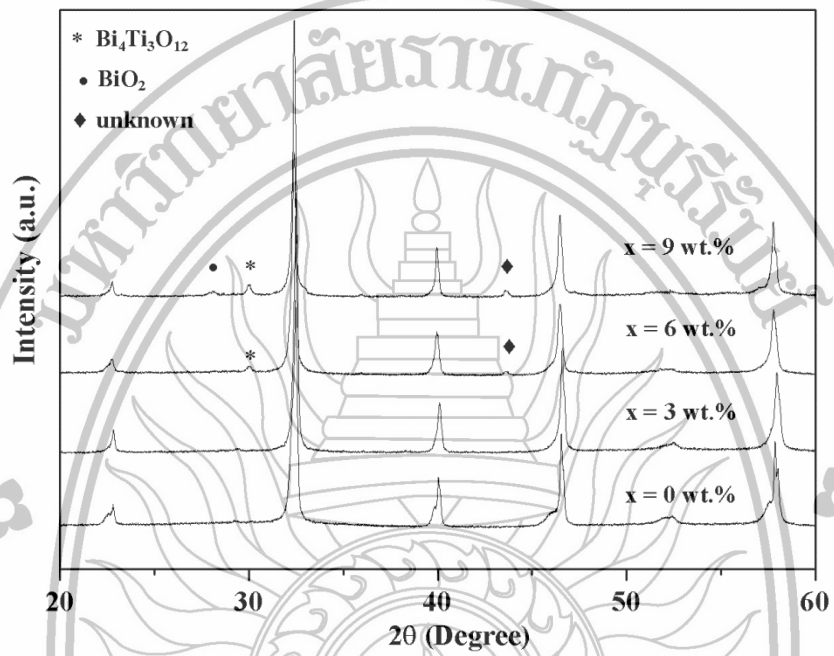

Figure 1. X-ray diffraction patterns of sintered ceramics with different x wt.%

4.2 Densification and Microstructure

In this research, the samples were sintered with different sintering temperature which produced the optimum density for each composition. The value of sintering temperature and optimum bulk density are displayed in Table 1. The bulk density decreased with increasing x wt.%andthe value was in range 5.769±0.021 to 5.583±0.025 g/cm^3 for x=0 to x=9wt.%.

Table 1
The optimum sintering temperature, the bulk density and the average grain size of composite ceramics

The Nb-Li additive (wt.%)	The optimum sintering temperature (°C)	The bulk density (g/cm^3)	The average grain size (μm)
0	1025	5.769±0.021	0.93± 0.14
3	1000	5.715±0.026	1.13 ± 0.20
6	925	5.707±0.018	0.63 ± 0.05
9	925	5.583±0.025	0.52 ± 0.07

Figure 2 shows microstructure of the as sintering composite ceramic samples. It can be observed the grain and the grain boundaries are obvious. The grain showscuboid like

shaped. The average grain sizes were 0.93 ± 0.14, 1.13 ± 0.20, 0.63 ± 0.05 and 0.52 ± 0.07for x=0, 3, 6 and 9 wt.%. It should be note that the grain size slightly decreased with increasing of x at the same sintering temperature from 0.63 ± 0.05 to 0.52 ± 0.07 μmfor x=6 to x=9 wt.%, respectively.

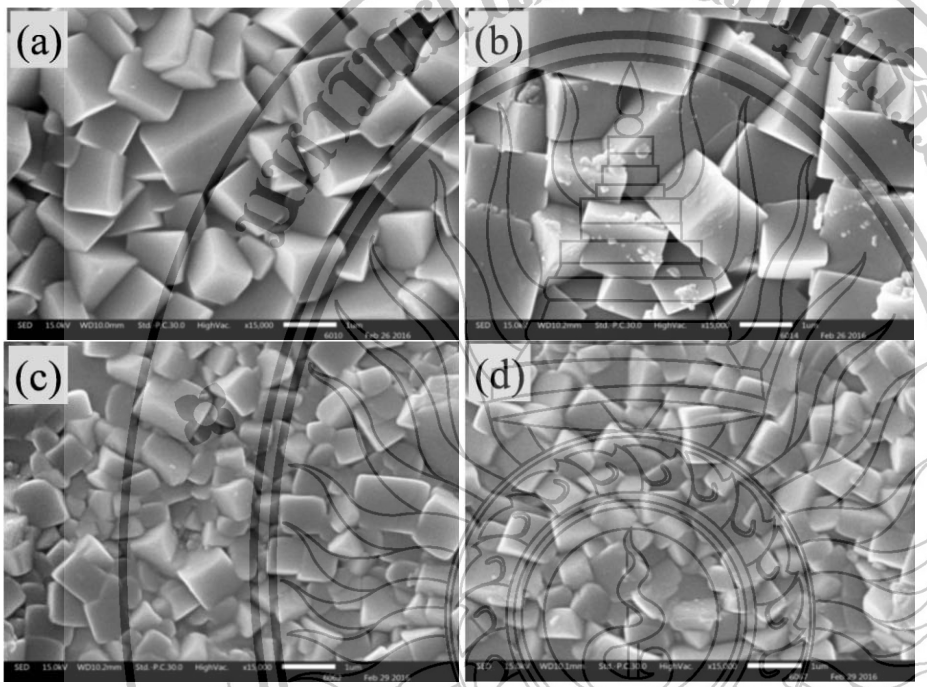

Figure 2. Scanning electron microscopy image for as sinter surface (a) x=0 wt.%, (b) x=3 wt.%,(c) x=6 wt.% and (d) x=9 wt.%

4.3 Mechanical properties

Effect of Nb_2O_5 and Li_2CO_3 wt.% on the mechanical properties of the composite ceramics was studied by Vickers and Knoopmicrohardness testers. Indentation was applied on the polished surface of studied samples. Applied load was 4.9 N with an indentation period of 10 s. Indentation diagonal and indentation crack length was measured for determination of Vickers hardness, Knoophardness Young's modulus and Fracture toughness. Figure 3 shows the samples after measurement Vickers hardness and Knoophardness tester. The value of Vickers hardness, Knoophardness Young's modulus and Fracture toughness shows in Table 2. The maximum Vickers and Knoop hardness were found at x=0 wt.% (5.33 ± 0.19 and 4.85 ± 0.18GPa, respectively). Base on these data, the Nb_2O_5 and Li_2CO_3 additive reduce both of Vickers and Knoop hardness properties. However, the value of Young's modulus and Fracture toughness of x=9 wt.% are maximum at 89.74 ± 5.62GPa and 2.98 ± 0.55MPa $m^{1/2}$, respectively.

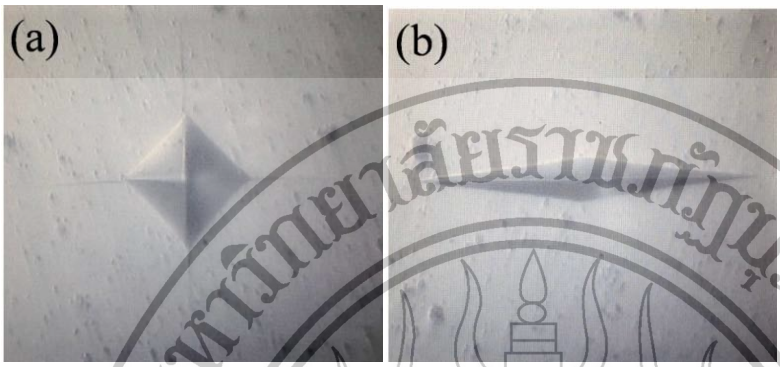

Figure 3. the surface sample aftermeasurement (a) Vickers hardness (b) Knoop hardnessat x=0 wt.%

Table 2
Mechanical properties of composite ceramics

The Nb-Li additive (wt.%) and optimum sintering temperature	Vickers hardness (GPa)	Knoop hardness (GPa)	Young's modulus (GPa)	Fracture toughness (MPa $m^{1/2}$)
0 @ 1025 °C	5.33 ± 0.19	4.85 ± 0.18	74.50 ± 7.45	1.22 ± 0.11
3 @ 1000 °C	3.31 ± 0.24	3.47 ± 0.35	71.28 ± 7.51	1.48 ± 0.28
6 @ 925 °C	5.20 ± 0.18	4.44 ± 0.25	55.43 ± 8.05	1.71 ± 0.29
9 @ 925 °C	4.92 ± 0.19	4.72 ± 0.19	89.74 ± 5.62	2.98 ± 0.55

5. Discussions

The following points based on the research results were discussed:

5.1 The single phase perovskite were found at x= 0 wt.%. It indicated that the synthesis method is suitable and low cost for fabrication this ceramic system. Beside, the single phase was found at x=3 wt.%. It should be note that the $Li^{+}$and Nb^{5+}ion diffused in to the lattice of $Bi_{0.5}(Na_{0.81}K_{0.19})_{0.5}TiO_3$ during sintering and limited for diffusion at this amount of the additive condition. However, the secondary phase can be observed at x=6 and 9 wt.%.There were detectable impurities or second phase such as $Bi_4Ti_3O_{12}$ in this research which is similar reported in previous works (Kim et al, 2007).It may cause by the substitution by Li^{+} and Nb^{5+} ion in A-site and B-site that leads to lattice distortion and fluctuation chemical components.

5.2 The increasing amount of the additive in composite ceramics reduced the bulk densityat each optimum sintering temperature (table 1). It may cause by inhomogeneous and closed poresincreased in ceramics. Moreover, the decreasing of grain sizes at x=6 and 9 wt.% indicated that the Nb_2O_5 and Li_2CO_3 played a role for grain growth inhibitor. The Nb_2O_5 and Li_2CO_3 at the grain boundary may be responsible for the decreased grain size and changes on the kinetics of grain growth.

5.3 The Young's modulus and fracture toughness properties were found maximum at x=9 wt.%. It may cause by the smallest grain size of this studied was achieved at this condition. The increasing of K_{IC} in this study was most likely due to the effect of reduced grain size. It should be note that residual stress might inhibit crack propagation in this study as reported by Jiansirisomboon et al (2008).

6. Conclusion

Lead-free composite ceramics of$Bi_{0.5}(Na_{0.81}K_{0.19})_{0.5}TiO_3$-x($Nb_2O_5$-$Li_2CO_3$) were fabricated by solid stated reaction technique. Effects of the additive on the properties of the studied ceramics were investigated. The additive is significant on phase formation, densification, microstructure and hardness. The densification decreased with adding amount of Nb_2O_5-Li_2CO_3 contents. However, this additive improves Young's modulus and fracture toughness properties. Base on this result suggested that this additive may be an effective on physical and mechanical properties on other ferroelectric lead free ceramics.

7. Recommendations

The following are recommendations base on the research results:

7.1 The improvement may be achieved by increasing the density of the material in this study by using techniques such as rate control sintering and Multi-step sintering.

7.2 Further work on the electrical characterization especially the dielectric and ferroelectric measurement of the composite ceramics in this study would facilitate a deeper understanding.

Acknowledgements

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