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Final manuscript

**Effect of lanthanum substitution on microstructure and electrical properties of
(Bi_{0.5}Na_{0.5})_{1-1.5x}La_xTi_{0.41}Zr_{0.59}O₃ ceramics**

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Abstract

Bismuth sodium zirconate (BNZ) based ceramics with a composition of (Bi_{0.5}Na_{0.5})_{1-1.5x}La_xTi_{0.41}Zr_{0.59}O₃ where x = 0, 0.005, 0.01, 0.02 and 0.03 were prepared by a solid-state mixed oxide method and sintered at the temperature of 900°C for 2 h. All the samples had relative density between 91 -97% of their theoretical values. Phase analysis using X-ray diffraction indicated single rhombohedral or pseudo-cubic perovskite structure. SEM micrographs showed that addition of La caused the average grain size of the BNTZ ceramics to decrease as well as an improvement of sample density. Dielectric properties at room temperature measured at 10 kHz indicated that addition of La increased the dielectric constant. The results of ferroelectric characterization also revealed that adding La caused a decrease in coercive field without affecting the remanent polarization.

Keywords: D. BLNZT; C. Electrical properties; C. Dielectric properties; D. Perovskites



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We are pleased to inform you that your manuscript entitled, "Physical and Electrical properties of Nb doped $\text{Bi}_{0.5}\text{Na}_{0.5}[\text{Zr}_{0.59}\text{Ti}_{0.41}]\text{O}_3$ " (2e-P02) has been accepted for publication in the proceedings of AMEC-7, *Ceramics International*.

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Physical and Electrical Properties of Nb doped $\text{Bi}_{0.5}\text{Na}_{0.5}[\text{Zr}_{0.59}\text{Ti}_{0.41}]\text{O}_3$

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Abstract

This research studied the effect of Nb doping on $\text{Bi}_{0.5}\text{Na}_{0.5}[\text{Ti}_{0.41}\text{Zr}_{0.59}]\text{O}_3$ (when Nb concentration = 0.00, 0.01, 0.03, 0.05, 0.07 and 0.09 mole fraction). Nb doped BNTZ ceramics were fabricated using a conventional mixed-oxide method. All samples were calcined at a temperature of 700 °C for 2 h and sintered at a temperature of 900 °C for 2 h. X-ray diffraction patterns suggested that the compounds possessed rhombohedral perovskite structure. SEM micrographs indicated that average grain size decreased as the amount of Nb additives increased. The electrical resistivity showed a decreasing trend with increasing Nb concentration due to excess charge present in the sample. The

dielectric constant and dielectric loss of samples showed no particular trend when Nb was added but the optimum was observed when 0.05-0.07 Nb mole fraction was present in BNTZ ceramics. In this study, both microstructure and donor-type effects played an important role in determining electrical resistivity and dielectric properties of these ceramics.

Keywords: D. Bismuth sodium titanate; B. X-ray method; C. Dielectric properties; C. Electrical properties.



Grain growth behavior in bismuth titanate-based ceramics

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Abstract

Bismuth titanate and lanthanum-doped bismuth titanate ceramics were prepared from freeze-dried powders employing conventional solid state reaction and sintering procedures. The sintering process was carried out at 1150 °C from 4 up to 48 h. X-ray diffraction analysis showed that preferred orientation was reduced in bismuth titanate ceramic as sintering time increased while lanthanum-doped sample showed much less degree of preferred orientation and was independent of sintering time. Grain growth studies also showed that initial anisotropic grain growth rate was the main factor controlling the grain morphology, rendering the plate-shaped grain in both pure and lanthanum-doped bismuth titanate ceramics. Based on established grain growth law, pore-controlled diffusion could be the major mechanism determining the observed microstructure in these layered compounds.

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Keywords: Sintering; Grain growth; Powders-solid state reaction; Bismuth titanate-based compound

1. Introduction

Pure and doped bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$ or BIT) have been under investigation recently due to their good electrical fatigue resistance behavior and their possible use in ferroelectric random access memories or FRAM applications.¹ A number of techniques have been employed to synthesize these materials both in thin film and ceramic forms.^{2–6} For thin films, a number of research work have shown that highly *c*-axis oriented grain morphology could be produced by several processing techniques particularly the templated grain growth method which enabled measurements of anisotropic properties of these films.^{7–10}

In ceramics, it has been well known that both pure and doped BIT possess plate-like grains and properties which are also orientation dependent. For example, dielectric properties along the direction perpendicular and parallel to *c*-axis were found to be quite different.¹¹ Hence, due to anisotropic behavior of this material, a number of researchers have fabricated BIT ceramics with grains aligned in certain direction by various techniques such as templated grain growth and tape-casting.¹² Others have found that employing external parameters such as

magnetic field or pressure could also produce ceramics with oriented grains.^{11–14} Inoue et al.¹² had shown that BIT ceramics with highly oriented grains could be fabricated from compacted plate-shaped powders which were originally prepared from salt solutions. However, the prepared ceramics contained large pores between well sintered plate-shaped grain colonies.¹² The authors also briefly mentioned the anisotropic grain growth behavior of sintered green compact prepared from conventionally prepared BIT powder. Based on these previous studies and the fact that grain growth kinetics and time dependence of grain morphology of BIT ceramics prepared by conventional sintering method have not been investigated in detail, this research therefore attempts to quantitatively study the effects of sintering time on microstructures, grain orientation and density of BIT ceramics. The results are discussed and compared to those of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) ceramics to elucidate the effects of lanthanum ion addition on grain growth behavior of BIT ceramics.

2. Experimental procedure

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ powders were prepared from binary oxides i.e. Bi_2O_3 (>98.0%, Fluka), La_2O_3 (99.99%, Cerac) and TiO_2 (>99%, Riedel-de Haën). The stoichiometric amounts of starting powders were mixed using ball milling with

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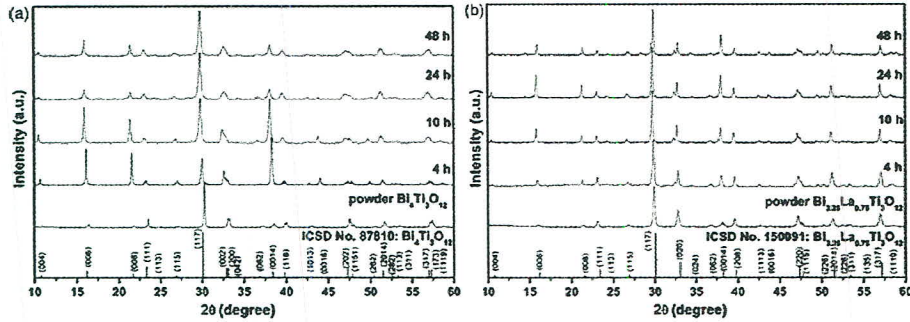


Fig. 1. X-ray diffraction patterns of calcined powder and sintered ceramics of (a) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and (b) $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$.

zirconia balls and distilled water for 24 h at a rate of 60 rpm. The mixtures were then transferred to a spherical flask and placed in a shell freezer. The flask was rotated in an ethanol bath for at least 1 h to produce frozen slurry, which was immediately dried in a vacuum drier for at least 24 h. After all ice was sublimated, fine freeze-dried powders were obtained. The powders were then calcined at 750 °C for 4 h before being re-ground, pressed into small pellets and sintered at 1150 °C for 4, 10, 24 and 48 h. X-ray diffraction analysis was employed to study phase formation and crystal structure of calcined powder and polished surfaces of ceramics using an X-ray diffractometer (Philips model X-pert) with $\text{CuK}\alpha$ radiation. Density was measured using Archimedes method. Microstructure of ceramic surfaces thermally etched in air at 1000 °C for 15 min was investigated using a scanning electron microscope (JEOL JSM-6335F). Grain size was obtained from SEM micrographs using direct measurement of grain length and thickness across the center of each grain. Averaged values for each sample were obtained from measuring one hundred grains. For degree of grain orientation, the following equations were used

$$P_0 = \frac{\sum I_0(00l)}{\sum I_0(hkl)} \quad (1)$$

$$P = \frac{\sum I(00l)}{\sum I(hkl)} \quad (2)$$

In the above equations, P_0 and P are the fraction of (00l) X-ray peaks with respect to all peaks for powders and ceramics, respectively. $I_0(00l)$ and $I(00l)$ are the integrated X-ray 00l peak intensities of powder and ceramic samples, respectively. $I_0(hkl)$ and $I(hkl)$ are their corresponding integrated intensities of all peaks within the 2θ range (i.e. 10–60°) under investigation. After P_0 and P were calculated, a Lotgering factor¹⁵ was obtained using equation

$$F = \frac{P - P_0}{1 - P_0} \quad (3)$$

3. Results and discussion

Fig. 1(a) shows X-ray diffraction patterns of BIT ceramics. For sintering time of 4 h, the ceramic surface showed relatively

high degree of preferred orientation of 00l-type indices. As the sintering time increased, the degree of preferred orientation decreased. Quantitatively, the 00l-oriented grain contribution approximated from integrated intensity of X-ray peaks relative to other grain orientation is also shown in Fig. 2. It seems therefore that for short sintering time (4 and 10 h), the compacted particles with c-axis oriented parallel to the pressing direction tended to grow and contribute to high degree of 00l preferred orientation observed. At longer sintering time (24 and 48 h), the influence of grains with c-axis oriented perpendicular to pressing direction became more pronounced (Fig. 1(a)) with a corresponding reduction in 00l preferred orientation (Fig. 2). These grains seemed to grow over some of the 00l-oriented grains, hence rendering smaller fraction of the latter on the ceramic surface. It should be noted that a slight shift of X-ray peaks of BIT ceramics compared to that of powder was probably due to instrumental error since the weight loss during sintering was found to be negligible, indicating that stoichiometry did not change and, therefore, X-ray patterns of ceramics and powder should be identical.

Fig. 1(b) shows X-ray diffraction of BLT calcined powder and sintered ceramics. Although the X-ray pattern of calcined

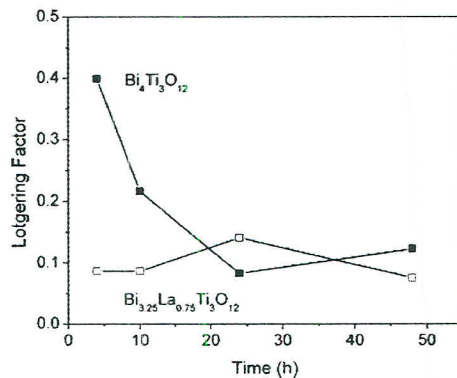


Fig. 2. Lotgering factor as a function of sintering time for BIT and BLT ceramics with respect to their calcined powders.

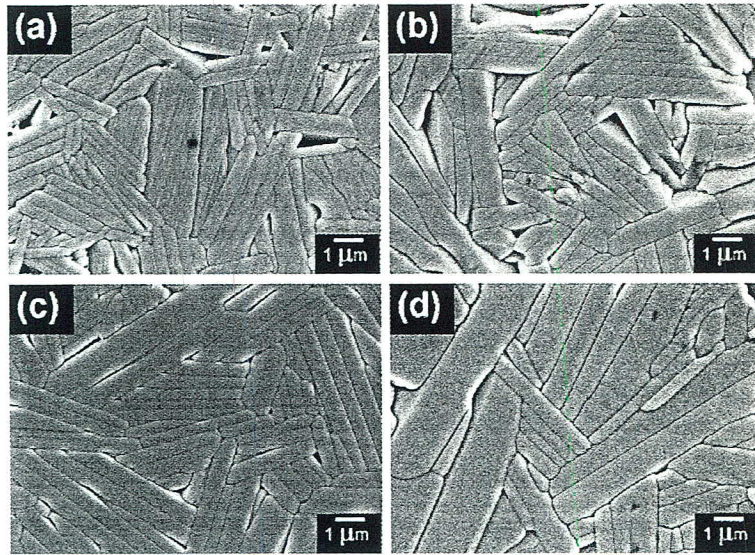


Fig. 3. SEM micrographs of thermally etched surfaces of BIT ceramics at various sintering times: (a) 4 h, (b) 10 h, (c) 24 h and (d) 48 h.

BLT powder was nearly the same as that of BIT, it could be seen that the degree of $00l$ preferred orientation of BLT ceramics was much less than that of BIT ceramics when compared at the same sintering time. The effect of sintering time on degree of preferred orientation based on calculated Lotgering factor of $00l$ -oriented

grains is also shown in Fig. 2. It could be seen that, compared to BIT ceramics, the degree of grain orientation of BLT was nearly independent of sintering time. For long sintering period, the degree of $00l$ -type preferred orientation in BIT and BLT ceramics was nearly the same. This suggested that the grain

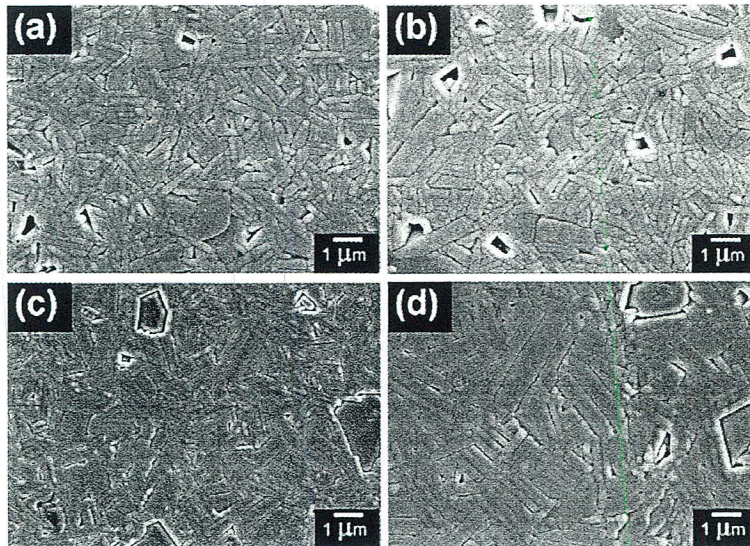


Fig. 4. SEM micrographs of thermally etched surfaces of BLT ceramics at various sintering times: (a) 4 h, (b) 10 h, (c) 24 h and (d) 48 h.

Table 1
Grain length and thickness of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$.

Sintering time (h)	Grain length: l (μm)		Grain thickness: t (μm)		l/t	
	BIT	BLT	BIT	BLT	BIT	BLT
4	5.88 ± 1.99	2.15 ± 0.73	0.98 ± 0.30	0.54 ± 0.13	6.00	3.98
10	8.44 ± 2.58	2.33 ± 0.66	1.46 ± 0.46	0.62 ± 0.16	5.78	3.74
24	9.62 ± 3.96	2.81 ± 1.00	1.67 ± 0.57	0.63 ± 0.15	5.76	4.45
48	10.38 ± 4.82	3.01 ± 1.21	1.77 ± 0.64	0.73 ± 0.21	5.86	4.12

Table 2
Density of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramics.

Sintering time (h)	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$		$\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$	
	Density (g/cm^3)	Relative density ^a (%)	Density (g/cm^3)	Relative density ^a (%)
4	7.55 ± 0.01	94.15	7.40 ± 0.03	96.47
10	7.41 ± 0.08	92.40	7.43 ± 0.02	96.88
24	7.31 ± 0.01	91.14	7.44 ± 0.03	96.95
48	7.38 ± 0.01	92.00	7.17 ± 0.13	93.51

^a X-ray density of $\text{Bi}_4\text{Ti}_3\text{O}_{12} = 8.02 \text{ g}/\text{cm}^3$ and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12} = 7.67 \text{ g}/\text{cm}^3$.

growth kinetics of these two systems might be similar at long sintering time.

Figs. 3 and 4 show thermally etched surfaces of BIT and BLT ceramics, respectively. For the same sintering time, the grain size of BIT was much larger than that of BLT ceramic. As the sintering time increased, the grain size became increased both in terms of grain length and thickness. Their values are listed in Table 1. The density for both compounds did not vary much with sintering time (see Table 2). It could be observed however that the relative density of BIT ceramics was slightly less than that of BLT due to the larger plate-like grains, causing greater difficulties in having high packing density. Their low density values were also confirmed in the micrographs in which relatively high fraction of large pores was observed in BIT compared to that of BLT ceramics.

To study grain growth behavior in these compounds, the grain size in terms of grain length and thickness as a function of time was plotted and shown in Fig. 5. It could be observed that,

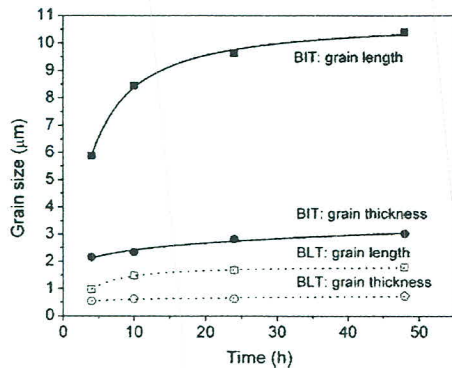


Fig. 5. Grain size of BIT and BLT ceramics as a function of sintering time.

in both BIT and BLT ceramics, the grain size along ab -plane initially increased abruptly and then increased more slowly at longer sintering time. Regardless of sintering time, both grain length and thickness of BIT ceramics were much larger than that of BLT ceramics. This indicates the well known effect of grain growth inhibition by lanthanum ions. To further quantify this point, the grain growth rate was obtained by fitting an empirical curve to the data points. It was found that the best fitted curve was obtained using the power function in the form $G = abt^{1-c}/(1 + bt^{1-c})$, where G is the grain size (length or thickness), t is the time, and a , b , c are the fitting constants. After the fitting, the slope was calculated to obtain instantaneous grain growth rate.

Fig. 6 shows the growth rate as a function of sintering time. It is apparent that the initial growth rate along ab -plane (grain length) was much faster than that along c -axis (grain thickness) for both BIT and BLT ceramics. This grain growth anisotropy could be largely due to the different atomic attachment/diffusion

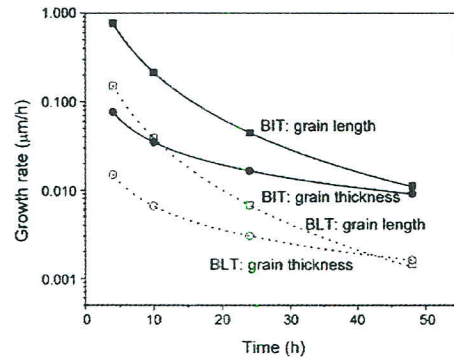


Fig. 6. Grain growth rate of BIT and BLT ceramics as a function of sintering time.

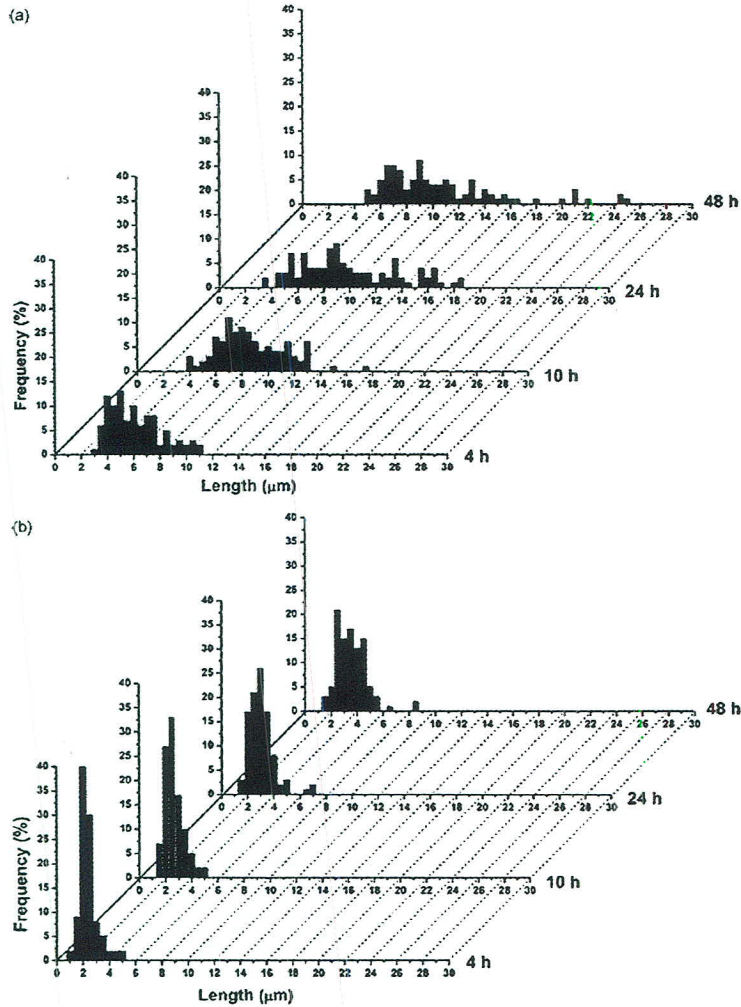


Fig. 7. Grain size distribution as a function of sintering time: (a) BIT and (b) BLT ceramics.

rates along different directions which, in turn, were influenced by the orthorhombic crystal structure of BIT and BLT. From the figure, it could be observed that the grain growth rate of BIT ceramic in both directions was about 10 times faster than that of BLT ceramic. This further proved the effectiveness of lanthanum in grain growth inhibition. As the sintering time increased, the growth rates in both directions decreased until their values became comparable at long sintering time. This reduction in grain growth rate should be expected since as the grain grew, more time would be needed to complete each atomic layer on each grain. This comparable grain growth along *ab*-plane and *c*-axis at long sintering time in both BIT and BLT ceramics also seemed to play a large part in determining the

amount of preferred orientation in these ceramics. Hence, the initial anisotropic grain growth rate seemed to be the main factor causing the plate-shaped microstructures in both BIT and BLT ceramics. For long sintering time, the grain growth rate became more isotropic with reduced preferred orientation as observed in this study. The effect of lanthanum on grain growth inhibition also resulted in narrower grain size distribution in BLT ceramics compared to that of BIT ceramics, as shown in Fig. 7.

In terms of grain growth mechanism in BIT and BLT ceramics, attempts to find the values of exponent *m* in the grain growth law i.e. having a relationship $G^m - G_0^m = kt$,¹⁶ where G_0 is grain size at time $t=0$ and k is a constant, were not very successful. Fig. 8 shows the plot of a straight line fit through data

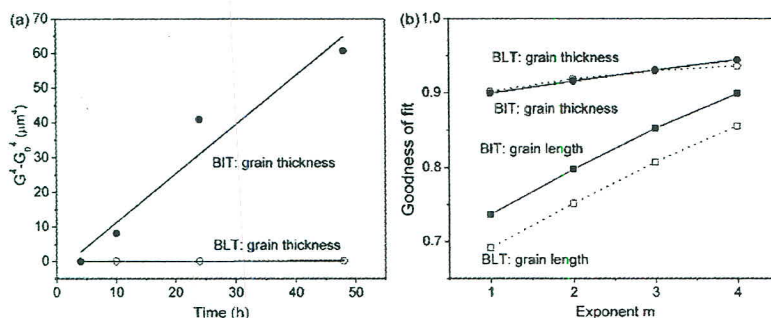


Fig. 8. Grain growth law applied to BIT and BLT ceramics: (a) linear fitting for $m=4$ and (b) goodness of fit as a function of exponent m .

points (using $m=4$ in this case) and the goodness of fit (having an ideal value of 1) as a function of exponent m . It could be seen that the best fit, though still having relatively large residual error, was found for m equals 4 which corresponded to the pore-controlled surface diffusion or boundary-controlled diffusion due to coalescence of second phase.¹⁶ However, the samples investigated in this study were mostly single phase so it was unlikely that the latter mechanism would play much role. Hence, pore-controlled surface diffusion may be a major mechanism in this material. Care should be taken however that other diffusion mechanisms may also play a role in these materials. The difficulties in applying grain growth law to BIT and BLT ceramics were due to the fact that these materials possessed anisotropic grain growth behavior as well as the fact that the grain growth law was established based on the assumption that the material must be a homogeneous compact with isotropic grain boundary energy and isolated spherical pores at the grain boundary. These properties were not closely followed in BIT and BLT ceramics due to their un-equiaxed grains. Nevertheless, based on the information obtained in this study, the rate controlling factors of grain growth could be the interfacial energy as well as the mobility of lanthanum ions. Further detailed investigation of lanthanum ion diffusion in BIT ceramic would be beneficial.

4. Conclusions

The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramics sintered at various sintering times up to 48 h were successfully fabricated. X-ray diffraction analysis showed that while $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics showed greater 001-type preferred orientation than $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramics at short sintering time, both materials had similar degree of 001-type preferred orientation at longer sintering period. In both $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramics, the anisotropic grain growth rate was observed at short sintering period while at long sintering time, the growth rate along ab - and c -plane became comparable. This study showed that the plate-shaped morphology in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramics was mainly the results of initial anisotropic grain growth rate. Sintering these ceramics at longer time could render a material with more isotropic microstructure with reduced preferred orientation.

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Dielectric and Piezoelectric Properties of Zirconium-Doped Bismuth Sodium Titanate Ceramics

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Keywords: BNT, dielectric, piezoelectric, solid solution

Abstract. Zirconium-doped bismuth sodium titanate ceramics were prepared using the conventional processing method. X-ray diffraction analysis indicated the materials were single phase with a systematic shift due to increased unit cell size. The measured densities and grain size of the ceramic samples were found to range from 5.79-6.03 g/cm³ and 0.5-1.6 μ m, respectively. The dielectric constant as a function of temperature became broader as Zr content increased. The piezoelectric constant was found to decrease with increasing Zr. Within the range of the solid solutions investigated, the materials seem to be promising for high temperature applications where stable dielectric constant is required.

Introduction

It is well known that a number of solid solution systems in ferroelectric ceramics are scientifically and technologically important. These include Pb(Zr,Ti)O₃, Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ and Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃, which have already been widely used in many sensor and actuator applications [1, 2]. However, the lead-containing compounds are currently of environmental concerns for future devices. Therefore, a number of non-lead material systems have been investigated in order to find suitable replacement for lead-based compounds. One of these non-lead systems is the solid solution of BaTiO₃-BaZrO₃ (BZT) which was found to possess high dielectric constant, low loss, high-strain capability and large piezoelectric coefficient [3-9].

Besides BZT, bismuth sodium titanate having chemical formula, Bi_{0.5}Na_{0.5}TiO₃ or BNT, has recently been received more attention due to their interesting ferroelectric properties. These include remanent polarization of 38 μ C/cm², coercive field of 73 kV/cm and high Curie temperature (T_c = 320 °C) [10-13]. Although a number of dopants have been used to modify properties of BNT ceramics [13-15], the solid solution Bi_{0.5}Na_{0.5}(Ti,Zr)O₃ have not yet been investigated in detail.

In this paper, the effects of Zr concentration on physical, dielectric and piezoelectric properties of BNT are studied and discussed.

Experimental

Bi_{0.5}Na_{0.5}Ti_{1-x}Zr_xO₃ (where x = 0, 0.05, 0.10, 0.15 and 0.20) powders were prepared from binary oxides, i.e. Bi₂O₃ (>98%, Fluka), Na₂CO₃ (99.5%, Carlo Erba), TiO₂ (>99%, Riedel-de Haën) and ZrO₂ (>99%, Fluka). The powder mixtures were ball-milled for 24 h using zirconia milling media in ethanol prior to calcination in alumina crucible at 800 °C for 2 h. After phase analysis by X-ray diffraction technique (XRD, JDX-8030), the powders were pressed into small pellets and sintered at 1100 °C for 2 h. The sintered ceramics were characterized for their densities using Archimedes method. The surface morphologies were studied using a scanning electron microscope (JEOL JSM-5910LV) and the grain size was obtained using a linear interception method. The dielectric constant as a function of temperature was measured using an LCR HITESTER connected to a high temperature furnace. The piezoelectric constant was measured using a d₃₃-meter (KCF PM-3001) after polling each sample for 5 minutes in 60 °C silicone oil under 40 kV/cm electric field.

Results and Discussion

X-ray diffraction patterns of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ (BNTZ) calcined powders and sintered ceramics are shown in Fig.1. For samples having the same composition, there was virtually no difference between X-ray patterns of powders and ceramics. The X-ray diffraction pattern of undoped BNT indicated the rhombohedral crystal structure, in agreement with the standard powder diffraction file no. 36-0340 and the pattern reported in literature [13,15]. Incorporation of Zr ions into BNT lattice caused a slight systematic shift of X-ray patterns to the left without changing relative peak intensities which suggested that the rhombohedral structure was maintained while the size of unit cell increased with increasing amount of Zr. Similar increase in lattice parameter was also observed for Zr-doped BaTiO_3 due to the larger Zr-ion substitution in Ti^{4+} site [16].

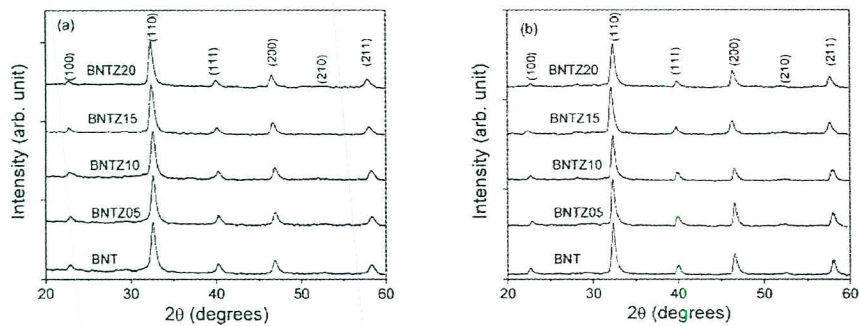


Figure 1. X-ray diffraction patterns of BNTZ: (a) calcined powder and (b) sintered ceramics

The density and the average grain size of BNT and BNTZ ceramics are listed in Table 1. The densities were within the range of 5.79-6.03 g/cm^3 , corresponding to the relative density of at least 95% of theoretical value. The average grain size ranged from 0.5-1.6 μm and increased with increasing Zr content. This indicated that the addition of ZrO_2 did not significantly affect the microstructures of BNTZ ceramics compared with that of BNT.

Table 1. Some room temperature properties of BNTZ ceramics.

	BNT	BNTZ05	BNTZ10	BNTZ15	BNTZ20
Density (g/cm^3)	5.95	5.79	5.94	5.93	6.03
Grain size (μm)	0.5	1.0	1.1	1.2	1.6
d_{33} (pC/N)	68	57	52	47	40
ϵ_r	524	620	655	572	562
$\tan \delta$	0.06	0.04	0.04	0.04	0.05

The dielectric constant and dielectric loss plotted as a function of temperature at 10 kHz are shown in Fig. 2. The dielectric curve for BNT showed a normal behavior and had the maximum value at 320 $^{\circ}\text{C}$, which was the transition temperature commonly found by other researchers [10-15]. The room temperature dielectric constant value of BNT (see Table 1) agreed well with the values reported [13-15]. The room temperature dielectric constant slightly increased with increasing Zr content up to 10 mol%Zr and then decreased with further addition of Zr. Unlike the BaTiO_3 - BaZrO_3

system [8,9] where addition of Zr decreased the T_c of the ceramics, the effect of Zr on the transition temperature of BNTZ was rather small.

In Fig. 2, it can be seen that increasing Zr concentration caused the dielectric-temperature curves to become more diffused with corresponding lower values of high-temperature dielectric constant. Since no frequency dependence of the dielectric constant was observed (not shown), the amount of Zr used in this study did not render the relaxor behavior of this material. This seems to be in agreement with the study on $\text{BaTiO}_3\text{-BaZrO}_3$ solid solution in which the frequency dependence of the dielectric constant was observed only when the amount of Zr used was equal to or greater than 30 mol% [8,9].

From Fig. 2 (b), except for BNTZ20, the dielectric loss of other BNTZ ceramics showed a relatively constant value for all samples up to about 150 °C. Above this temperature, the values slightly decreased and then increased as the loss became more significant at high temperature. This behavior was also observed in BZT system [8,9]. The room temperature dielectric loss values for BNTZ ceramics were comparable to that of BNT sample. The d_{33} piezoelectric constant of BNTZ showed a decreasing trend with increasing Zr content (see Table 1). It seems therefore that the random distribution of larger Zr ions inside BNT lattice caused some reduction in polarizability of material. It would be interesting, however, to further investigate the BNTZ system in order to find out whether the morphotropic phase boundary is present in order to obtain materials with good dielectric and piezoelectric properties following the PZT and BZT systems.

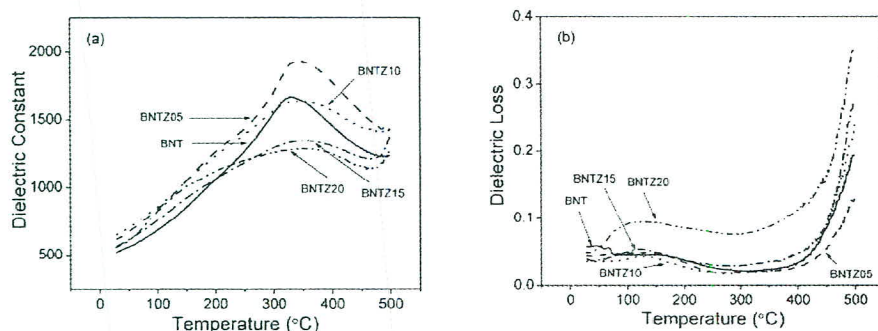


Figure 2. Graph of (a) dielectric constant and (b) dielectric loss of BNTZ ceramics at 10 kHz plotted as a function of temperature.

Summary

The single-phase $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ ceramics with x varied from 0 to 0.2 were successfully prepared using conventional ceramic processing method. X-ray diffraction analysis showed a single rhombohedral perovskite phase with systematic shift in peak position, indicating that substitution of Zr^{4+} ions into Ti^{4+} site caused lattice expansion. The piezoelectric coefficient (d_{33}) showed a decreasing trend while the dielectric constant-temperature curves showed a broader peak with increasing Zr concentration. This seems to suggest that the material might be used as a high-stability dielectric material.

Acknowledgments

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ผลงานตีพิมพ์ในวารสารวิชาการระดับชาติ

Synthesis of Lead-Free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ Powder

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Abstract

In this study, an approach to synthesize bismuth sodium zirconate powders with the formula $\text{Na}_{0.5}\text{Bi}_{0.5}\text{ZrO}_3$ by mixed oxide method was investigated. The reaction involved mixtures of reagent grade Bi_2O_3 , Na_2CO_3 and ZrO_2 powders. The mixtures were calcined at temperatures in the range of 700 - 850°C, and the starting composition was also subsequently changed by addition of Bi_2O_3 , Na_2CO_3 or ZrO_2 powder at 5, 10 and 15 wt%. The calcined powders were analyzed using X-ray diffractometry. The result revealed that $\text{BNZ}/\text{Na}_2\text{CO}_3$ powders calcined at 800°C for 2 hours produced BNZ compound with maximum purity.

Key words: Lead-free ceramics, BNZ, Synthesis, Powder

Introduction

In the past, many electrical devices such as multilayer capacitors (MLCCs), piezoelectric transducers, pyroelectric detectors/sensors, electrostrictive actuators, precision micropositioners, MEMs, etc. were all made from lead bearing compounds, e.g. lead titanate (PbTiO_3), lead zirconate titanate ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$), lead magnesium niobate ($\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$), etc. However, volatilization of toxic PbO during high-temperature sintering causes environmental pollution.⁽⁴⁾ Nowadays, several studies have attempted to find non-lead ceramics which may replace lead-based ceramics.⁽⁷⁾ Examples are barium titanate (BaTiO_3), sodium niobate (NaNbO_3), bismuth potassium titanate ($\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$) Nakata, *et al.*⁽⁵⁾, bismuth lithium titanate ($\text{Bi}_{0.5}\text{Li}_{0.5}\text{TiO}_3$), bismuth sodium titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$), etc. Recently, bismuth sodium titanate (BNT) has received particular attention because of its interesting ferroelectricity at room temperature and high Curie temperature at 320°C. This solid solution was discovered by Smolenskii, *et al.*⁽⁸⁾ and has been studied further by a number of researchers.^(2-3, 6, 8) On the other hand, this material had drawbacks such as high coercive field ($E_c = 73 \text{ kV/cm}$) and high conductivity, resulting in the difficulty in poling process.⁽⁹⁾ Many researchers also attempted to improve microstructure, mechanical properties, piezoelectric and electrical properties. Zirconium is one of many elements used as a modifier for the development of well-known $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ and $\text{Ba}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ceramics. Watcharapasorn, *et al.*⁽⁹⁾ attempted to study this problem by investigating $\text{Bi}_{0.5}\text{Na}_{0.5}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ with $x = 0, 0.05, 0.1, 0.15$ and

0.20. The result revealed that the density, grain size and hardness were increased with increasing Zr contents. The purpose of this study is to synthesize a new lead-free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ in which Ti was totally replaced by Zr and various conditions such as calcination temperature and starting compositions were varied to investigate their effect on compound formation.

Materials and Experimental Procedures

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ (BNZ) powders were prepared by the conventional mixed oxide method. The starting chemicals used were Bi_2O_3 (99.9%, Aldrich), Na_2CO_3 (99.5-100.5%, RdH) and ZrO_2 (99%, Riedel-de Haën). The starting powders were weighed and ball milled in ethanol for 24 hours. The slurry was dried at 120°C for 24 hours. The mixed powders contained in alumina crucible were calcined at temperature ranging from 700 - 850°C for 2 hours. Then, the calcined powders were checked by X-ray diffraction method technique to find the appropriate temperature. After that, the starting composition which was subsequently changed by addition of Bi_2O_3 , Na_2CO_3 or ZrO_2 powder at 5, 10 and 15 wt% was prepared by above process and then it was calcined at the appropriate temperature. Finally, the calcined powders were investigated once more by using an X-ray diffractometer and measurement of the amount of second phases was performed.

Results and Discussion

After as-mixed $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ (BNZ) powder was calcined at different temperatures, phase

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formation was investigated by XRD as shown in Figure 1. From the results, it was found that the temperatures in range of 700°C - 750°C were not enough for completing the reaction. X-ray diffraction analysis showed that the sample contained a large amount of second phases. On the other hand, BNZ powders calcined at 850°C indicated that the materials began to partially react with alumina crucible and produced less pure BNZ powder. Therefore, based on this study, optimized calcination temperature was found to be 800°C. Figure 2 showed that the second phases appeared in range of $2\theta = 25 - 30, 33, 46$ and 50° which were most likely the phases of Bi_2O_3 and ZrO_2 . However, Na_2CO_3 phase was not exhibited at temperature above 600°C.⁽¹⁾ It was expected therefore that addition of Na_2CO_3 should help complete the reaction. Hence, addition of 5, 10, 15 wt% Na_2CO_3 was carried out and the results are shown in X-ray patterns in Figure 3. The amount of second phases as indicated by a decrease in peak intensity in the region of 2θ from $25-30^\circ$ was clearly observed. Although both Na_2CO_3 and Bi_2O_3 have low melting point i.e. 850 and 820°C, respectively, the volatilization of Na_2CO_3 is not as well known as Bi_2O_3 . In this study, it showed that Na_2CO_3 volatilized more than Bi_2O_3 and/or had dissociation problem at calcination temperature used. In order to check this hypothesis, Bi_2O_3 and ZrO_2 were also separately added into starting mixture. Figures 4 and 5 showed X-ray diffraction results of adding these two compounds, respectively. It showed that both Bi_2O_3 and ZrO_2 had nearly no effect on phase formation of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$. This seemed to be in agreement with the existing second phases observed in Figure 2. The amount of second phases approximated from X-ray peak analysis of calcined powders with separately added Na_2CO_3 , Bi_2O_3 and ZrO_2 are shown in Table 1. It was found that the relative concentration of impurity phase was ≈ 10.7 wt% in un-doped BNZ powder. These phases were decreased with increasing Na_2CO_3 content. However, at 15 wt% Na_2CO_3 content, it showed the second phase reduction was not significantly different from 10 wt% Na_2CO_3 . For separate

addition of Bi_2O_3 and ZrO_2 in BNZ powder, both can be seen that the amount of second phases clearly increased when compared with BNZ powder without their addition. Thus, from these results, reduction of second phases by using Na_2CO_3 additive could be confirmed. Hence, based on this study, the calcination temperature of 800°C and addition of excess Na_2CO_3 improved BNZ phase purity. Further improvement of phase purity by re-calcination and changing calcination time will be carried out and reported in the near future.

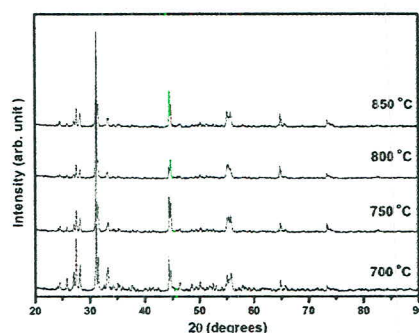


Figure 1. XRD patterns of BNZ powders calcined at different temperature for 2 hours.

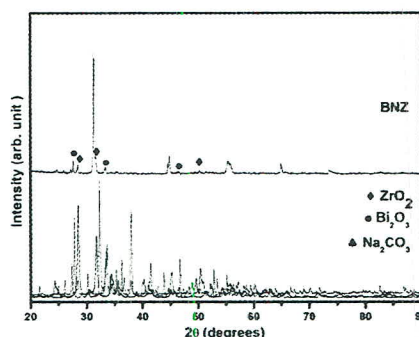


Figure 2. XRD pattern of BNZ powder calcined at 800°C for 2 hours compared with starting powder XRD pattern.

Table 1. amount of second phases of BNZ/ Na_2CO_3 , BNZ/ Bi_2O_3 and BNZ/ ZrO_2 powders.

Amount of addition (%wt)	Second phases (%wt) of BNZ/ Na_2CO_3	Second phases (%wt) of BNZ/ Bi_2O_3	Second phases (%wt) of BNZ/ ZrO_2
0	10.69	10.69	10.69
5	9.76	26.77	24.11
10	9.33	43.98	39.78
15	9.36	44.10	43.53

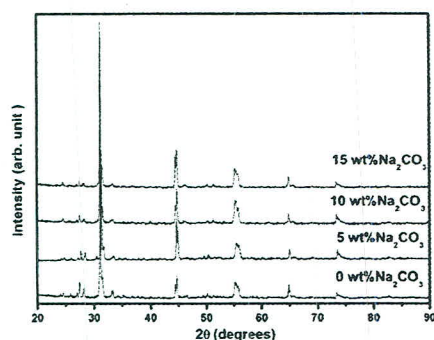


Figure 3. XRD patterns of BNZ/ Na_2CO_3 powders calcined at 800°C for 2 hours.

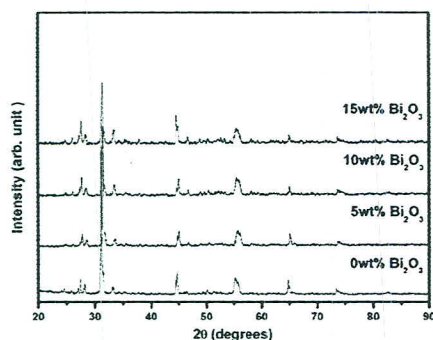


Figure 4. XRD patterns of BNZ/ Bi_2O_3 powders calcined at 800°C for 2 hours.

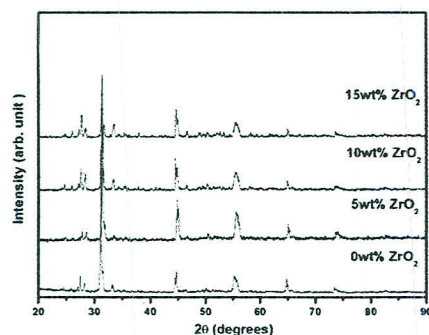


Figure 5. XRD patterns of BNZ/ ZrO_2 powders calcined at 800°C for 2 hours.

Conclusions

This research studied several factors affecting phase formation of new lead-free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ compound. Optimized conditions included calcination temperature of 800°C for 2 hours with addition of excess Na_2CO_3 .

Acknowledgments

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Microstructures and Mechanical Properties of Lead-Free Bismuth Sodium Titanate Zirconate Ceramics

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Abstract

Lead-free bismuth sodium titanate zirconate ceramics ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ where $x = 0.20, 0.35, 0.40, 0.45, 0.60$ and 0.80) were fabricated using a conventional mixed-oxide method. All samples were calcined at temperatures ranging from 700 – 800°C for 2 h and sintered at a temperature of 900°C for 2 h. Higher sintering temperatures caused the ceramics, particularly those containing high Zr content, to melt and/or react with alumina crucible. The density of BNTZ ceramics was found to be in the range of 5.1 – 6.1 g/cm^3 . Since the density values were found to increase with Zr concentration, it seemed that the ability to use low sintering temperature in this study was likely to be due to the lower melting point of ceramics with possible partial aid from very small amount of second liquid phase present as detected by X-ray diffraction analysis. SEM micrographs indicated a presence of small grains embedded between large grains especially in high Zr containing samples, causing a rather wide grain size distribution. Average grain size of BNTZ ceramics was found to range from 0.8 to $5.4\text{ }\mu\text{m}$. In terms of mechanical properties, their dependence on Zr concentration was not obvious. Knoop hardness of BNTZ samples ranged from 2.8 – 4.8 GPa while Vickers showed the values of 3.2 – 5.4 GPa . Fracture toughness of these ceramics was found to be in the range of 1.1 – $2.9\text{ MPa}\cdot\text{m}^{1/2}$. These values were comparable to those of commercialized and widely investigated PZT and PLZT ceramics.

Background

It is well known that currently the PZT-based solid solutions have been widely used as actuators, transducers and sensors due to their excellent piezoelectric properties [1–3]. Currently, many other materials that possess high dielectric and piezoelectric coefficients still contain lead ions, for example, PMN-PT and PZN-PT [1–3]. Due to environmental concerns, many attempts to study non-lead systems with comparable electrical properties to those of lead-based ones have been carried out. Starting with $\text{Ba}(\text{Ti,Zr})\text{O}_3$ solid solutions, several investigators have shown that these systems possessed broad dielectric constant-temperature curves indicating that addition of Zr into BaTiO_3 produced more diffused phase transition [4,5]. In addition, above $30\text{ mol}\%$ Zr, the material showed relaxor behavior and these materials seemed to be suitable for tunable capacitors applications. The purpose of the present study is to investigate the microstructure and mechanical properties for bismuth sodium titanate zirconate ceramics fabricated by using conventional mixed-oxide method.

Materials and Methods

The $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ ceramics with $x = 0.20, 0.35, 0.40, 0.45, 0.60$ and 0.80 were prepared by mixed oxide method powders. The starting powders of Bi_2O_3 ($>98\%$, Fluka), Na_2CO_3 (99.5% , Carlo Erba), TiO_2 ($>99\%$, Riedel de Haën) and ZrO_2 ($>99\%$, Riedel de Haën) were mixed in

ethanol using zirconia ball milling media. After drying, the calcination was carried out at $800^\circ\text{C}/2\text{h}$ for composition $x = 0.20, 0.35, 0.40$ and 0.45 , and at $700^\circ\text{C}/2\text{h}$ for composition $x = 0.60$ and 0.80 . The calcined powders were then ball milled again for 6 h . Phase development and crystallographic structure of the powders were examined by X-ray diffraction. The calcined powders were uniaxially pressed into the pellets before being sintered at 900°C for 2 hours and re-checked for phase purity using X-ray diffraction technique. For microstructural investigation, the ceramics were polished and thermally etched at 800°C for 15 minutes.

The density and microstructure of ceramics were evaluated by Archimedes method and scanning electron microscopy (SEM), respectively. The theoretical density was approximated from the unit cell size and its constituent ions with an assumption that the lattice type remained the same and only the lattice parameter changed with composition. The grain size was determined from the SEM micrograph using mean linear interception. The well-polished ceramics were subjected to Knoop (Matsuzawa MXT- α) and Vickers (Galileo Microscan 2) indentations for hardness (i.e. H_v and H_k) measurements. Young's modulus (E) and fracture toughness (K_{IC}) were determined following method described by Antais et al. [5] and Marshall et al. [6]. SEM images of indented areas were employed to determine all of these mechanical properties.

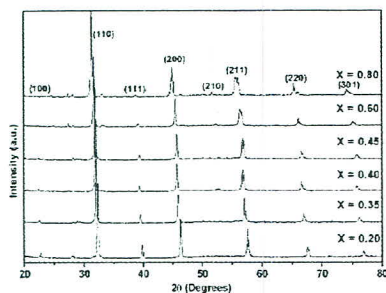


Fig.1 XRD pattern of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ ceramics.

Results and Discussion

X-ray diffraction pattern of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ (where $x = 0.20, 0.35, 0.40, 0.45, 0.60$ and 0.80) ceramics were shown in Fig. 1. It can be seen the peaks of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$ systematically shifted to the left. This indicated that the unit cell expanded. This is in agreement with the fact that the ionic size of Zr ion ($r_{\text{Zr}^{4+}} = 0.72 \text{ \AA}$) is larger than the ionic size of Ti ion ($r_{\text{Ti}^{4+}} = 0.61 \text{ \AA}$). Based on the relative intensities of X-ray diffraction peaks, one of the apparent features observed was the reduction in peak intensity of (100) and (111) reflections.

From preliminary investigation of crystal structure change due to the replacement of Zr in Ti lattices, it was found that the reduction of these reflections came from the differences in scattering factor and ionic size of Zr compared to those of Ti when the rhombohedral lattice was kept the same. This suggested that the lattice was distorted such that the reflecting planes of atoms for these reflections caused higher degree of destructive interference with increasing Zr concentration. Another observable feature was the splitting of X-ray peaks especially in the sample with $x = 0.60$ and 0.80 . From crystal structure investigation, if the unit cell expanded while maintaining the rhombohedral structure, this peak splitting seemed to be naturally occurred. Small amount of second phases was also present in the samples which could possibly be bismuth oxide or some Zr-rich phase based on SEM-EDS results. However, these second phases were not expected to have significant effects on mechanical properties of BNTZ ceramics.

The microstructures of the BNTZ ceramics are illustrated in Fig. 2. The density of sample with $x =$

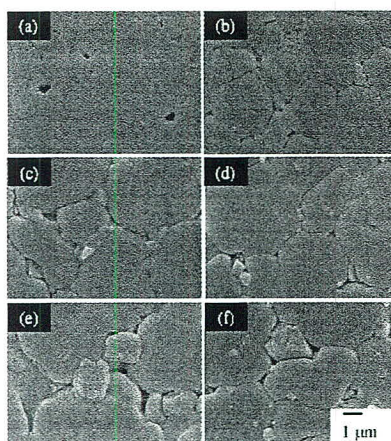


Fig.2 SEM micrograph of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ ceramics, where $x =$ (a) 0.20, (b) 0.35, (c) 0.40, (d) 0.45, (e) 0.60 and (f) 0.80

0.2 was relatively low compared to those containing higher Zr content. The density for most samples was found to be in the range of $5.9\text{--}6.1 \text{ g/cm}^3$ which corresponded to the relative density of at least 95% of their theoretical values. The average grain size was found to range from $0.8\text{--}5.4 \text{ μm}$. Although it seemed that the grain size increased with Zr content but the change was only observed in low-Zr sample. In high-Zr sample, nearly no change in grain size was observed but there was smaller grains along the grain boundaries of the matrix grains which could be part of the grain growth inhibition in high Zr sample. These smaller grains were found to be Zr-rich phase as determined from SEM-EDS technique.

Figure 3 shows backscattered electron images of representative BNTZ ceramic samples along with their corresponding EDS spectrum. It could be observed that relative intensity of Zr peaks were different between these two samples indicating the different amount of Zr present in the matrix phase. Despite the fact that there are some uncertainties associated with quantitative analysis using this technique, the EDS spectrum still gave higher concentration of Zr for $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_3$ sample than the one containing lower Zr content. This higher amount of substitution corresponded well to the shift in X-ray peaks.

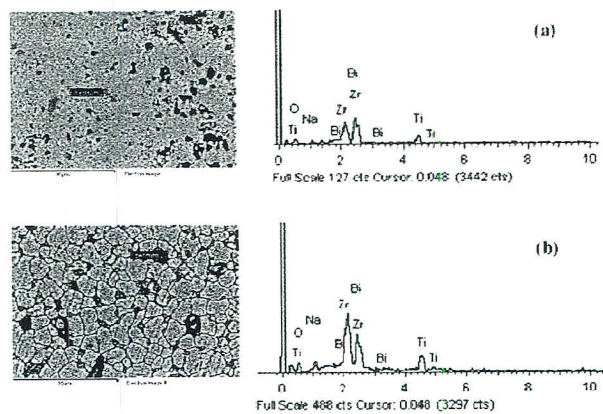


Fig.3 Backscattered electron images and EDS spectra of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ ceramics: (a) $x = 0.2$ and (b) $x = 0.8$.

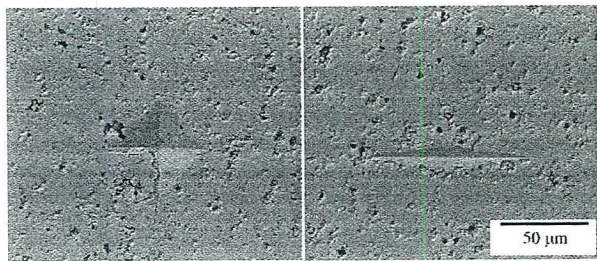


Fig.4 SEM micrograph of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ where $x=0.40$, showing (a) Vickers and (b) Knoop indentation impressions.

Table 1 Physical and mechanical property of BNTZ ceramics

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$	Density (g/cm^3)	Grain size (μm)	Mechanical property			
			H_K	H_V	$E(\text{GPa})$	$K_{IC} (\text{MPa m}^{1/2})$
0.20	5.1	0.78 ± 0.10	4.45 ± 0.49	4.33 ± 0.32	60	1.25
0.35	6.0	2.63 ± 0.17	3.63 ± 0.14	3.97 ± 0.26	89	1.34
0.40	5.9	5.37 ± 0.47	4.76 ± 0.62	5.24 ± 0.47	143	2.86
0.45	5.9	4.18 ± 0.29	2.78 ± 0.78	3.24 ± 0.50	63	1.06
0.60	6.0	4.77 ± 0.52	4.26 ± 0.10	5.44 ± 0.24	140	1.95
0.80	6.1	4.63 ± 0.38	3.17 ± 0.76	4.09 ± 0.16	110	1.49

Mechanical properties of the ceramics in terms of Knoop hardness (H_K), Vickers hardness (H_V), Young's modulus (E) and fracture toughness (K_{IC}) were investigated and their values are listed in Table 1. The hardness value dependence on Zr concentration was not obvious. The Knoop hardness was found to range from 2.8-4.8 GPa, while Vickers hardness was 3.2-5.4 GPa. The Young's modulus and fracture toughness were

found to be about 60-140 GPa and 1.1-2.9 $\text{MPam}^{1/2}$, respectively. Therefore, compared to the values obtained for the widely investigated PZT and PLZT ceramics which had the hardness and fracture toughness of about 3-5 GPa and 1.0-1.5 $\text{MPam}^{1/2}$ [1], the BNTZ ceramics seemed to possess good mechanical properties suitable for actuator applications.

Figure 4 shows Vickers and Knoop hardness indentation impressions of a BNTZ ceramic. Compared to the grain size, the indented area was much larger and therefore the variation in mechanical properties of the samples could be largely due to microstructural inhomogeneities. Further studies will be needed to separate the effect of grain boundaries from the grains themselves.

Conclusion

Lead-free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$ ceramics (where $x = 0.20, 0.35, 0.40, 0.45, 0.60$ and 0.80) were successfully fabricated. X-ray diffraction patterns showed a systematic shift to the left, indicating the expansion of unit cell when Zr concentration increased in agreement with ionic size consideration. All ceramic samples showed dense microstructure with grain size variation dependence on Zr content. The mechanical properties of BNTZ ceramics did not show significant dependence on composition. Nevertheless, their values especially the hardness and fracture toughness were found to be comparable to those of PZT and PLZT which suggested that these materials may be suitable for actuator applications.

Acknowledgements

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Commission on Higher Education (CHE). Authors would also like to thank the Graduate School and the Faculty of Science, Chiang Mai University.

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Poly(ethersulfone)s carrying pendant sulfonated imide side group. The first step in the preparation involved nitration of poly(ethersulfone) (ultrason[®]-S6010), with ammonium nitrate and trifluoroacetic anhydride resulting in the nitrated poly(ethersulfone) (NO₂-PES). In the second step, the nitro groups on polymer were reacted with tin(II)chloride and sodium iodide as reducing agents for creating the amino poly(ethersulfone) (NH₂-PES). The imide-poly(ethersulfone)s (IPES) were obtained by reaction of phthalic anhydride and the amino-poly(ethersulfone) with triethyl amine. The sulfonated imide-poly(ethersulfone)s (SIPES) were prepared by chlorosulfonic acid. The different degrees of sulfonated imide units of poly(ethersulfone) were successfully synthesized by an optimized condition. The Sulfonated imide-poly(ethersulfone)s (SIPES) were studied by FT-IR, ¹H-NMR spectroscopy and thermo gravimetric analysis (TGA). Sorption experiments were conducted to observe the interaction of sulfonated polymers with water. The ion exchange capacity (IEC) and proton conductivity of SIPES membranes were evaluated with increase of degree of sulfonation. The water uptake of synthesized SIPES membranes exhibit 30~65% compared with 28% of Nafion 211[®]. The SIPES membranes exhibit proton conductivities (25°C) of 1.21-2.62×10⁻³ S/cm compared with 3.37×10⁻³ S/cm of Nafion 211[®].

Keywords: Polyimide, Poly(ethersulfone), Membrane, PEMFC, Proton exchange membrane, Proton conductivity

P - A 37

Preparation of Bismuth Sodium Zirconate Powder by Mixed Oxide Method

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Lead-free bismuth sodium zirconate powder with formula Na_{0.5}Bi_{0.5}ZrO₃ was prepared by conventional mixed oxide method. Bismuth sodium zirconate (BNZ) powder with 10 wt% Na₂CO₃ was calcined at 800°C for 2 h dwell time. Investigation of the effects of re-calcination and dwell time on phase formation of powders was also carried out. The results revealed that re-calcination significantly affected the formation of single-phase BNZ powder. Phase characteristics were checked by X-ray diffraction (XRD). Powder cell software was employed to simulate crystal structure of BNZ powder. It was found that BNZ powder most likely possessed an orthorhombic structure. Microstructure and chemical composition were characterized by scanning electron microscopy (SEM) and energy-dispersive (EDX) techniques, respectively. Thermo-gravimetric analyzer (TGA) and differential scanning calorimetry (DSC) were used to study thermal transformation of starting compound. Relationships between these properties and phase formation were discussed in details.

Keywords: BNZ powder, Crystal structure, Lead-free powder, Preparation, Mixed oxide method

P - A 38

Preparation, Electrochemical Properties and Cytotoxicity Assessment of Nanosized CuO/La₂O₃/CeO₂ Composite for the Decomposition of Gaseous Ammonia

Chang-Mao Hung

Department of Vehicle Engineering, Yung-Ta Institute of Technology and Commerce, Taiwan

This work considers the CuO/La₂O₃/CeO₂ nano-rare earth composite materials were synthesized by coprecipitation method with aqueous solutions of copper nitrate, lanthanum nitrate and cerium nitrate. The performance of the selective catalytic oxidation of ammonia to N₂ (NH₃-SCO) over a CuO/La₂O₃/CeO₂ nano-rare earth composite materials in a tubular fixed-bed reactor (TFBR) at temperatures from 423 to 673 K in the presence of oxygen was reported. The catalytic redox behaviors were determined by cyclic voltammetry (CV). Further, cell cytotoxicity and the percentage cell survival were determined by using MTS assay on human fetal lung tissue cell (MRC-5). The experimental results show that the

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The Institute for Basic Science, Changwon National University
Jeju Special Self-Governing Province
Korea Tourism Organization

Keywords: Solar cells, III-V heterostructures, Fianite, YSZ, Antireflection coating

P - A 27

Influence of Ramp Time of Close Spaced Sublimation on Crystal Structure, Optical and Electrical Properties of CdTe Thin Films

Thitinaï Gaewdang, Ngarnit Wongcharoen, Waraporn Bunkua, Chanya Thaisatuen
School of Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang

CdTe thin films were deposited by close-spaced sublimation(CSS) method on glass substrate in vacuum at a pressure of 3.0×10^{-2} mbar. The samples were prepared under four ramp time conditions: 20, 30, 40 and 50 minutes. During this work, the temperature of the precursor and the substrate were fixed at 550 and 450°C respectively. Crystal structure of these films were checked by X-ray diffraction method. CdTe thin films are polycrystalline belonging to cubic structure with a preferential orientation of (111) plane. The grain size and surface morphology of the films was studied by using Scanning Electron Microscope (SEM). The biggest grain size about $8.16 \mu\text{m}$ were observed at ramp time 40 min. The optical transmission spectrum of CdTe thin films were performed by UV-Vis spectrophotometer with wavelength in the range 600~1,000 nm. Thus, energy gap value of each ramp time was obtained from the spectral transmission data. The electrical properties of CdTe thin films were performed by using dark current-voltage and light current-voltage measurements. The resistivity of the films around $1 \times 10^6 \Omega \cdot \text{cm}$ was observed at room temperature. Resistivity values of all samples decrease under illumination by ELH halogen lamp.

Keywords: CdTe thin films, Close-spaced sublimation, XRD

P - A 28

Investigation of Morphotropic Phase Boundary for Bi_{0.5}Na_{0.5}Ti_{1-x}Zr_xO₃ Solid Solutions by X-ray Diffraction Technique

Ampika Rachakorn, Anucha Watcharapasorn, Panupong Jaiban, Napatporn Petnoi, Sukanda Jiansirisomboon
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Binary solid solutions system of lead-free bismuth sodium titanate zirconate (Bi_{0.5}Na_{0.5}Zr_xTi_{1-x}O₃ or BNTZ) powders were prepared by a conventional mixed-oxide method with varied composition of $x = 0.40, 0.45, 0.50, 0.55, 0.60$ and 0.65 mole fraction. Preliminary X-ray diffraction analysis of BNTZ at low Zr ($x < 0.40$) showed the unit cell expansion while maintaining rhombohedral structure. At high Zr ($x > 0.60$) however, peak splitting occurred and this seemed to indicate a distorted tetragonal or orthorhombic structure. Thus, this study intended to investigation the existence of morphotropic phase boundary (MPB) using the change in crystal structure and graphical analysis based on X-ray diffraction patterns.

Keywords: BNT, BNZ, Morphotropic phase boundary, X-ray diffraction

P - A 29

Kinetic Study of CdS Thin Films Prepared by Chemical Bath Deposition Method and Their Characteristics for Solar Cell Applications

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2-e-P02

Preparation and Phase Transformation of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Zr}_x\text{Ti}_{1-x}\text{O}_3$

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In this research, lead-free bismuth sodium titanate zirconate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{Zr}_x\text{Ti}_{1-x}\text{O}_3$ or BNTZ) powders ($x = 0.20, 0.35, 0.40, 0.45, 0.60$ and 0.80 mole fraction) were prepared by a conventional mixed-oxide method by varying factor of time, temperature calcinations and excess Na_2CO_3 . Preliminary, X-ray diffraction analysis showed a systematic peak shift in the pattern indicating that the unit cell size increased with increasing Zr content. From crystal structure investigation, at low Zr concentration the unit cell expanded while maintaining rhombohedral structure. At high Zr concentration, however, peak splitting occurred and this seemed to indicate a distorted tetragonal structure. Thus, author was studied Quantitative analysis using Rietveld refinement analysis on X-ray diffraction pattern data of BNTZ powder were carried out in order to relate the crystallographic information to their ferroelectric and piezoelectric properties.

2-e-P03

Synthesis and Characterization of Bismuth Sodium Zirconate Powders

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In this study, an approach to synthesize bismuth sodium zirconate powders with a formula $\text{Na}_{0.5}\text{Bi}_{0.5}\text{ZrO}_3$ by mixed oxide method was investigated. Bismuth sodium zirconate (BNZ) powders were characterized by X – ray diffraction (XRD), scanning electron microscopy (SEM) and energy – dispersive X – ray (EDX) techniques. The effect of calcination temperature and dwell time on phase formation of the powders was examined. It was found that the calcination temperature and dwell time had a pronounced effect on phase formation of the calcined BNZ powders. Optimization of calcination conditions could produce single-phase $\text{Na}_{0.5}\text{Bi}_{0.5}\text{ZrO}_3$ having most likely a distorted tetragonal structure. Rietveld analysis was employed to characterize the exact crystal structure and its relationship to ferroelectric and piezoelectric properties.

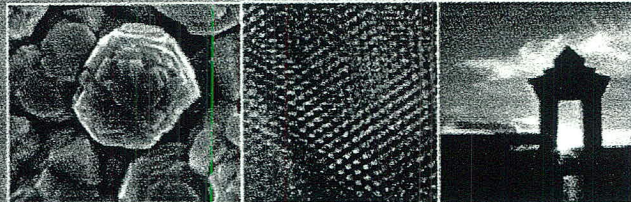
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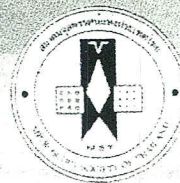
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Poster Presentation

Characteristics of Nb doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{0.41}\text{Zr}_{0.59}\text{O}_3$ Ceramics

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Abstract

Lead-free Nb doped Bismuth Sodium Titanate Zirconate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{0.41}\text{Zr}_{0.59}\text{O}_3$, BNTZ) ceramics with $x = 0, 0.01, 0.03, 0.07$ and 0.09 mole fraction was synthesized by the conventional mixed oxide method. All samples were calcined at 700°C for 2h, pressed into the pellet and sintered at 900°C for 2h. The BNTZ ceramics were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the crystal structure was rhombohedral phase. The SEM micrographs indicated the average grain sizes tended to decrease with increasing Nb concentration while the relative density values were at least 95% of theoretical value. In addition, the phases found in these ceramics were also identified using energy dispersive X-ray analysis (EDX). These information will be correlate to their measured properties.

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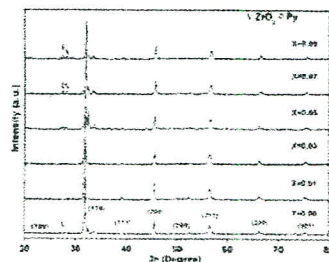


Figure 1 X-ray diffraction patterns of $[\text{Bi}_{0.5}\text{Na}_{0.5}(1-x)\text{Ti}_{0.41}\text{Zr}_{0.59}]_{1-x}\text{NbO}_3$ ceramics when $x = 0, 0.01, 0.03, 0.07$ and 0.09 , respectively.

Poster Presentation

Effects of Sintering Temperatures on Preparation of BNZ Ceramic

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Abstract

In this research, effects of sintering temperatures on preparation of lead-free bismuth sodium zirconate ceramic were investigated. BNZ powder with 10 wt% Na_2CO_3 was prepared by mixed oxide method. Phase characteristic of calcined powder was checked by X-ray diffraction technique. It was found that BNZ powder has an orthorhombically distorted perovskite (ABO_3) structure. Then, BNZ ceramics were fabricated by solid-state sintering and were sintered in a temperature range of 900 – 1100 °C for 2 h. From the results, BNZ ceramic sintered at 1050 °C showed maximum relative density. XRD patterns indicated that complete solid solution ceramic appeared at 900 and 950 °C. Non-perovskite phase existing in BNZ ceramics was found to be ZrO_2 . Scanning electron microscopy was used to study microstructure. It could be seen that grain growth of all BNZ ceramics increased with increasing sintering temperatures. However, evaporations of bismuth or sodium based composition seemed to affect grain growth and induced porosity in this system. Relationship between competing mechanism of evaporation and densification of BNZ ceramic were discussed in details.

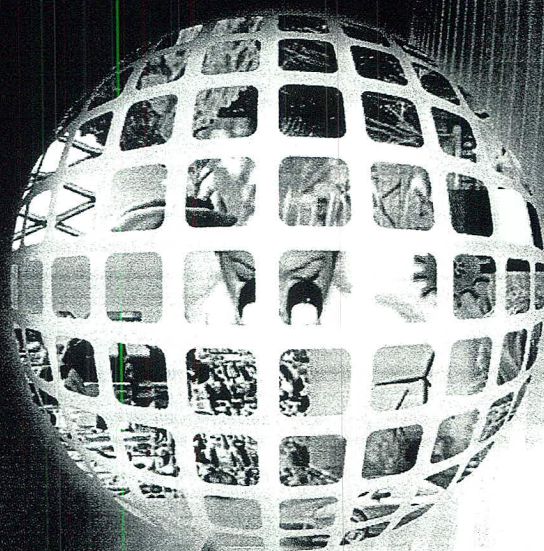
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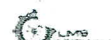
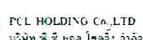
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Synthesis of Lead-free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ Powder

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Abstract

In this study, an approach to synthesize bismuth sodium zirconate powders with a formula $\text{Na}_{0.5}\text{Bi}_{0.5}\text{ZrO}_3$ by mixed oxide method was investigated. The reaction involved mixtures of reagent grade Bi_2O_3 , Na_2CO_3 and ZrO_2 powders. The mixtures were calcined at temperature in the range of 700 - 850 °C and the starting composition was also subsequently changed by addition of Bi_2O_3 , Na_2CO_3 or ZrO_2 powder at 5, 10 and 15 wt%. The calcined powders were analyzed using X-ray diffractometry. The result revealed that BNZ/ Na_2CO_3 powders calcined at 800 °C for 2 h produced BNZ compound with maximum purity.

Keywords: Lead-free ceramics; BNZ; Synthesis; Powder

1. Introduction

In the past, many electrical applications such as multilayer capacitors (MLCCs), piezoelectric transducers, pyroelectric detectors/sensors, electrostrictive actuators, precision micropositioners, MEMs, etc. were all lead bearing compounds, e.g. lead titanate (PbTiO_3), lead zirconate titanate ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$), lead magnesium niobate ($\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$), etc. However, volatilization of toxic PbO during high-temperature sintering causes environmental pollution [1]. Nowadays, several studies attempted to find non-lead ceramics which could replace lead-based ceramics. Examples were barium titanate (BaTiO_3), sodium niobate (NaNbO_3), bismuth potassium titanate ($\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$) [2], bismuth lithium titanate ($\text{Bi}_{0.5}\text{Li}_{0.5}\text{TiO}_3$), bismuth sodium titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$), etc. Recently, bismuth sodium titanate (BNT) has been widely studied

because of its interesting ferroelectricity at room temperature and high Curie temperature at 320 °C. This solid solution was discovered by Smolenskii *et al.* [3] and has been studied further by a number of researchers [3-6]. On the other hand, this material had drawbacks of high coercive field ($E_c = 73$ kV/cm) and high conductivity, resulting in the difficulty in poling process [7]. Many researchers attempted to improve microstructure, mechanical properties, piezoelectric and electrical properties. Zirconium is one of many elements used as a modifier for the development of well-known $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ and $\text{Ba}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ceramics. Watcharapasorn *et al.* [8] attempted to study this problem by investigating $\text{Bi}_{0.5}\text{Na}_{0.5}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ with $x = 0, 0.05, 0.1, 0.15$ and 0.20 . The result revealed that the density, grain size and hardness were increased with increasing Zr contents. The purpose of this study is to synthesize a new lead-free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ in which Ti was totally replaced by Zr and various conditions such as calcination temperature and starting compositions were varied to investigate their effect on compound formation.

2. Experimental procedures and methods

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ (BNZ) powders were prepared by the conventional mixed oxide method. The starting chemicals used were Bi_2O_3 (99.9%, Aldrich), Na_2CO_3 (99.5-100.5%, RdH) and ZrO_2 (99%, Riedel-de Haën). The starting powders were weighed and ball milled in ethanol for 24 h. The slurry was dried at 120 °C for 24 h. The mixed powders contained in alumina crucible were calcined at temperature ranging from 700 - 850 °C for 2

h. Then, the calcined powders were checked by X-ray diffraction method technique to find the appropriate temperature. Finally, the starting composition which was subsequently changed by addition of Bi_2O_3 , Na_2CO_3 or ZrO_2 powder at 5, 10 and 15 wt% was prepared by above process and then it was calcined at the appropriate temperature. The calcined powders were investigated once more by using X-ray diffractometer.

3. Results and discussion

After as-mixed $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ (BNZ) powder was calcined at different temperatures, phase formation was investigated by XRD as shown in Fig. 1. From the results, it was found that the temperatures in range of 700 °C - 750 °C were not enough for completing the reaction. X-ray diffraction analysis showed that the sample contained a large amount of second phases. On the other hand, BNZ powders calcined at 850 °C indicated that the materials began to partially react with alumina crucible and produced less pure BNZ powder. Therefore, based on this study, optimized calcination temperature was found to be 800 °C. Figure 2 showed that the second phases appeared in range of $2\theta = 25 - 30$, 33, 46 and 50° which were most likely to be the phases of Bi_2O_3 and ZrO_2 . It was expected therefore that addition of Na_2CO_3 should help complete the reaction. Hence, addition of 5, 10, 15 wt% Na_2CO_3 was carried out and the results are shown in X-ray patterns in Fig. 3. The amount of second phases by a decrease in peak intensity in the region of 2θ from 25-30° was clearly observed. Although both Na_2CO_3 and Bi_2O_3 have low melting point i.e. 850 and 820 °C, respectively, the volatilization of Na_2CO_3 is not as well known as Bi_2O_3 . In this study, it showed that Na_2CO_3 might be more volatile than Bi_2O_3 and/or had dissociation problem at calcination temperature used. In order to check this hypothesis, Bi_2O_3 and ZrO_2 were also separately added into starting mixture. Figure 4 and 5 showed X-ray diffraction results of adding these two compounds, respectively. It showed that both Bi_2O_3 and ZrO_2 had nearly no effect on phase formation of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$. This seemed to be in agreement with the

existing second phases observed in Fig. 2. Hence, based on this study, the calcination temperature of 800 °C and addition of excess Na_2CO_3 both affected phase purity of synthesized compound. Further improvement of phase purity by re-calcination and changing calcination time will be carried out and reported in the near future.

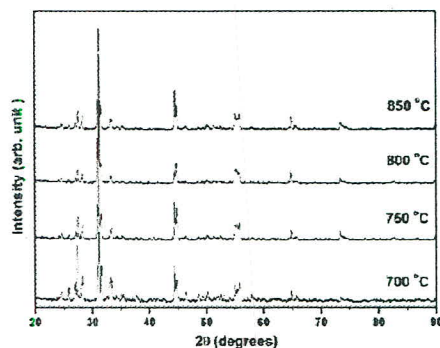


Figure 1. XRD patterns of BNZ powders calcined at different temperature for 2 h.

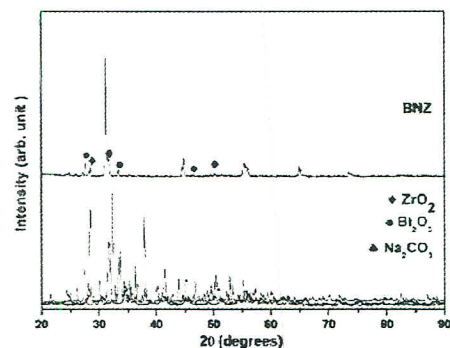


Figure 2. XRD pattern of BNZ powder calcined at 800 °C for 2 h compared with starting powder XRD pattern.

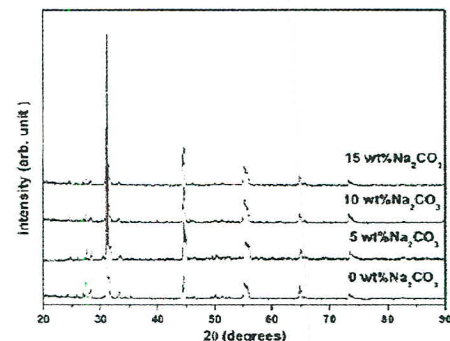


Figure 3. XRD patterns of BNZ/ Na_2CO_3 powders calcined at 800 °C for 2 h.

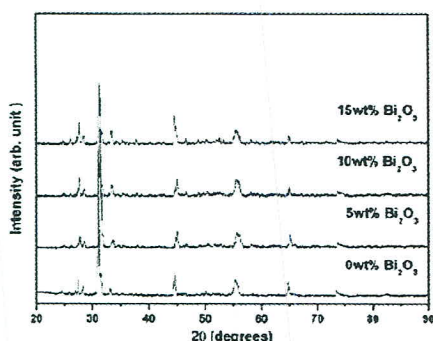


Figure 4. XRD patterns of BNZ/ Bi_2O_3 powders calcined at 800 °C for 2 h.

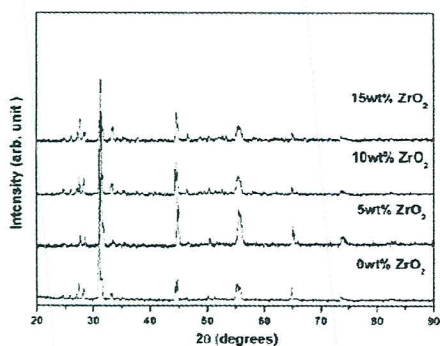


Figure 5. XRD patterns of BNZ/ ZrO_2 powders calcined at 800 °C for 2 h.

4. Conclusion

This research studied several factors affecting phase formation of new lead-free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ compound. Optimized conditions included calcination temperature of 800 °C for 2 h with addition of excess Na_2CO_3 .

5. Acknowledgment

This work is supported by the Thailand Research Fund (TRF), the Commission on Higher Education (CHE). We would also like to acknowledge financial support from the TRF through the Royal Golden Jubilee Ph.D. (RGJ) program.

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Abstracts

THE 36th CONGRESS
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การประชุมวิชาการวิทยาศาสตร์
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Abstract: In this work, effect of sintering temperature and W^{6+} doping content on phase, densification and microstructure of $Bi_{1.25}La_{0.75}(Ti_{1-x}W_x)_2O_{12}$ or BLTW ceramics when $x = 0, 0.01, 0.03, 0.05, 0.07, 0.09$ and 0.10 , was investigated. The BLTW ceramics were sintered at $1000-1150^\circ\text{C}$ for 4 h. The result of phase analysis by X-ray diffraction indicated the existence of orthorhombic phase for all sintering temperatures. At low WO_3 doping content (≤ 0.01 mol) showed small increase of particular set of plane $\{001\}$. Microstructure of BLTW ceramics showed plate-like grains with random orientation. Increase in WO_3 doping concentration reduced both grain size and degree of preferred orientation of the grains. Increasing the WO_3 content decreased densification of the ceramics. The microstructural result was well corresponded to the X-ray diffraction result.

E0038: Effects of calcination temperature and excess Na_2CO_3 on phase characteristics of bismuth sodium zirconate powder

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Abstract: This research studied the effects of calcination temperature and excess Na_2CO_3 on phase characteristics of bismuth sodium zirconate powder. $Bi_{0.5}Na_{0.5}ZrO_3$ powder was prepared by mixed oxide method. The calcination temperature used was in a range of $700 - 850^\circ\text{C}$. After that, the starting compositions were changed by adding Na_2CO_3 in the amount of 0, 5, 10, 15, 20, 25 and 30 wt%. Phase characteristics of powders were analyzed using X-ray diffraction technique. The second phases appearing in BNTZ powder were Bi_2O_3 and ZrO_2 starting powders. These phases were decreased with increasing Na_2CO_3 addition.

E0039: Effects of Nb_2O_5 on microstructure, phase, and densification of bismuth sodium titanate ceramics

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Abstract: In this research, the effects of Nb_2O_5 (0, 1, 5, 10, 15 and 20 mol%) on microstructure, phase, and densification of bismuth sodium titanate [$(Bi_{0.5}Na_{0.5})TiO_3$ or BNT] ceramics were studied. The powder for making BNT ceramics was prepared by a conventional solid state reaction method. Using calcinations temperature of 800°C for 2 h. After uniaxial pressing of the powder into discs, green samples were sintered at 1450°C for 2 h. The results showed that the solubility limit of Nb_2O_5 in the BNT system could be as high as 20 mol%. The density of the ceramics tended to increase with Nb_2O_5 addition up to 5 mol% and then, density of the ceramics was slightly reduced. The grain size showed a decreasing trend with increasing Nb_2O_5 concentration. These results indicated that suitable amount of Nb_2O_5 addition could help improve densification and reduce grain growth in BNT ceramics.

E0040: Effect of calcination time on phase formation of $Bi_{0.5}Na_{0.5}Ti_{1-x}Zr_xO_3$

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Abstract: The $Bi_{0.5}Na_{0.5}Ti_{1-x}Zr_xO_3$ solid solutions when $x = 0.20, 0.35, 0.40, 0.45, 0.60$ and 0.80 mole fraction were prepared using a conventional mixed-oxide method. The raw materials were mixed in ethanol using zirconia ball media for 24 h. The calcination temperature was at 700°C and 2 h dwell time. Phase formation of the powders was examined by X-ray diffraction. The XRD patterns demonstrated nearly all samples possessed rhombohedral structure with increasing Zr concentration, all peaks systematically shifted to the left indicated that the unit cell expanded in agreement with larger Zr^{4+} ions were substituting smaller Ti^{4+} ions. At Zr additives up to 0.60 and 0.80 mole fraction secondary phases appeared which could possibly be Zr-rich phase. Thus, the experimental procedure to decrease the amount of secondary phase using increasing dwell time of calcination from 2 h to 4 h. The results showed those secondary phases were slightly reduced. In addition, it was hypothesized that besides varying dwell time, changing temperature and heating/cooling rate of calcination should further increase phase purity of BNTZ powder.



Abstracts

THE 35th CONGRESS on SCIENCE and TECHNOLOGY of THAILAND (STT 35)

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nanofiber. If these patterns were used as a scaffold, it mimicked the fibrillar structure of collagen in nature having nonwoven and aligned fiber, on extracellular matrix. Extracellular matrix (ECM) is a structure surrounding and supporting cells which composed of ground substance or proteoglycan and collagen fibers which embedded as a 3D network in proteoglycan.

E_E0005 PROTEIN ANALYSIS BY MALDI-TOF MS USING PLA NANOFIBER MAT SUPPORTS FOR PROTEIN ABSORPTION.

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Abstract: Various PLA nanofiber patterns were successfully fabricated. This paper showed 3 patterns having different on aligned fiber mats. L3, L4 and L6 exhibited %alignment of 39, 66 and 35, respectively. When these nanofiber mat patterns were used for support standard Pepmix-1, having 5 proteins; angiotensin II, angiotensin I, neurotensin, ACTH[1-17], ACTH[18-39], for MALDI-TOF MS investigation, it was found that the L4 pattern exhibited the highest intensity peaks of protein and the less S/N ratio. This is because L4 contained high aligned fiber, resulting large surface area, and enhancing protein adsorption.

E_E0006 EFFECT OF EXCESS Pb CONTENT AND ANNEALING TEMPERATURE ON PHASE EVOLUTION IN THIN FILMS PZT

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Abstract: This research studies effect of annealing temperature and excess Pb addition on phase of the films lead zirconate titanate (PZT). Sol PZT was synthesized using a modified triol sol-gel processing method. PZT films were prepared by spin coating on (111) platinized silicon substrate. Phase of PZT thin films were investigated using X-ray diffraction technique. The experimental results showed that annealing temperature and excess Pb content were found to affect on phase and orientation of PZT thin films. The results indicated that (111) PZT orientation started to present after being annealed at 400°C and its intensity reduced with increasing annealing temperature. On the other hand, at annealing temperature $\geq 500^\circ\text{C}$, (001) and (110) orientations tended to increase with increasing annealing temperature. However, pyrochlore phase still appeared even though at annealing temperature 650°C. Increase in excess Pb addition was found to increase crystalline phase, with affected the stability of perovskite crystallization in PZT thin films.

E_E0007 GRAIN GROWTH AND CRYSTALLOGRAPHIC ORIENTATION OF Mo⁶⁺-DOPED BLT CERAMICS

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Abstract: In this work, effect of Mo⁶⁺ doping concentration on morphology, growth and crystalline orientation on bismuth lanthanum titanate grain, i.e. Bi_{3.25}La_{0.75}(Ti_{1-x}Mo_x)₂O₁₂ (BLTM); when $x = 0, 0.01, 0.03, 0.05, 0.07, 0.09$ and 0.1 mol, respectively. The BLTM powder were prepared by mixed-oxide method and calcined at 750 °C for 4 h dwell time before being pressed and sintered at 1000-1150°C for 4 h. The result showed that BLTM ceramics composed of plate-like grains. Increase in Mo⁶⁺ doping concentration increased both grain size and degree of preferred orientation of the grains. The result of microstructural investigation was found to be well agreed with observed X-ray diffraction patterns.

E_E0008 PHYSICAL AND DIELECTRIC PROPERTIES OF LEAD-FREE BISMUTH SODIUM TITANATE ZIRCONATE CERAMICS

Ampika Rachakom, Sukanda Jiansirisomboon and Anucha Watcharapasorn

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Abstract: This research studied phase formation, microstructure and dielectric properties of lead-free bismuth sodium titanate zirconate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{Ti}_{1-x}\text{Zr}_x\text{O}_3$, BNTZ) ceramics when $x = 0.20, 0.35, 0.40, 0.45, 0.60$ and 0.80 mole fraction, respectively. BNTZ powders were prepared by the conventional mixed oxide method. The synthesized powders were pressed and sintered at 900°C for 2 h. The experimental results suggested that BNTZ ceramics still possessed rhombohedral phase with the relative density of 95 % of theoretical value. The grain size seemed to increase with Zr content. In terms of dielectric properties, it was found that addition of Zr caused a decreasing trend in dielectric constant. It was postulated that the expansion of unit cell was the main cause in changing the electrical properties.

E E0009 EFFECT OF BNT ADDITION ON PHYSICAL AND DIELECTRIC PROPERTIES OF PZT CERAMICS

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Abstract: This research studied effect of bismuth sodium titanate (BNT) addition on physical and dielectric properties of lead zirconate titanate (PZT) ceramics. The BNT additional content used in this study were 0, 0.1, 0.5, 1.0 and 3.0 wt%. The ceramics were sintered at $1050\text{--}1200^\circ\text{C}$ in atmosphere. Density, microstructure and phase identifications were carried out using Archimedes' method, scanning electron microscopy and X-ray diffraction technique, respectively. Electrical properties such as dielectric constant and dielectric loss at room temperature were also measured. The results showed that density and grain size of the ceramics tended to decrease with increasing content of BNT addition. Dielectric constant and dielectric loss of the ceramics, however, were found to increase with increasing of BNT content.

E E0010 EFFECT OF CuO NANO-PARTICULATES ADDITION ON PHASE AND MICROSTRUCTURE OF PZT CERAMICS

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Abstract: This research studies effect of CuO nano-particulates addition on phase and microstructure of PZT ceramics. Firstly, PZT/xCuO powders were prepared using a mixed oxide method, when $x = 0, 0.1, 0.5$ and 1 wt%. The powders were then pressed and sintered at 1250°C for 2 h. PZT/xCuO were investigated in term of phase, density and microstructure using X-ray diffraction technique, Archimedes's method and scanning electron microscope, respectively. The results showed that tetragonality and density of PZT ceramics increased with 0.1 wt% CuO addition. Both parameters, however, tended to decrease with further increase in CuO content. Average grain size was found to sharply decrease with only 0.1 wt% CuO addition.

E E0011 EFFECT OF Si_3N_4 NANO-PARTICLES ON PHASE AND MICROSTRUCTURE OF BaTiO_3 CERAMICS

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Abstract: This research studies effect of Si_3N_4 nano-particle on phase and microstructure of BaTiO_3 ceramics. $\text{BaTiO}_3/\text{xSi}_3\text{N}_4$ powders; $x = 0, 0.1, 0.5, 1$ and 3 wt% were prepared, pressed and sintered at temperature 1400°C for 2 h. The $\text{BaTiO}_3/\text{xSi}_3\text{N}_4$ ceramics were investigated in terms of phase, density and microstructure using X-ray diffraction technique, Archimedes's method and scanning electron microscope, respectively. The experimental results indicated crystal structure changes, i.e. tetragonality tended to increase, while relative density of the ceramics with 0.1 wt% Si_3N_4 addition was maximum. However, the relative density tended to reduce with increasing content of $\text{Si}_3\text{N}_4 > 0.1$ wt%. Average grain size was found to increase with increasing content of added Si_3N_4 nano-particles.

E E0012 FABRICATION, ELECTRICAL AND MECHANICAL PROPERTIES OF PZT/PVDF 0-3 COMPOITES

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Abstract: This research studied fabrication and properties of $x\text{PZT}/(1-x)\text{PVDF}$ composites with $x = 0, 0.05, 0.1, 0.2, 0.3, 0.4$ and 0.5 volume fraction. The experimental results indicated that densities of the composites tended to increase with increasing PZT ceramic content. Investigation of phase and microstructure of the composites revealed well dispersion of PZT in PVDF phase. Dielectric measurement of the composites showed that the dielectric constant increased with increasing of PZT phase, while dielectric loss tangent value reduced. The maximum value of dielectric constant was found in $0.5\text{PZT}/0.5\text{PVDF}$ composite ($\epsilon_r \approx 96$). The results of mechanical measurements in terms of hardness, Young's modulus and fracture toughness were found to be improved with increase in PZT content.

E_E0013 STUDY ON MELT SPINNING OF POLY (METHYL METHACRYLATE) FIBER FOR OPTIC APPLICATIONS

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Abstract: Melt spinning of poly(methyl methacrylate) fibers was studied for its potential use in optical PMMA fibers were made, using single screw extruder, under different spinning conditions: extruding temperatures, throughputs rates, and draw ratios to investigate their effects on fiber spinnability and optical properties. Experimental results showed that best spinnability was obtained at extruding temperature 270°C and throughput rate 8 rpm such that fibers could be spun continuously without breakage. Poor fiber spinnability was obtained at low extruding temperature (230°C) as fiber breakage occurred quite often. This is thought to be due to higher stress acting on fibers when low temperature was employed. PMMA fibers obtained showed good light transmission, thus, have potential for applications on optics in new areas, including decoration and clothing.

E_E0014 FABRICATION OF LEAD-FREE BISMUTH SODIUM ZIRCONATE CERAMICS

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Abstract: This research studied fabrication of lead-free bismuth sodium zirconate ceramics with formula $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$. The $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ ceramic powder was prepared using a mixed-oxide method and checked for phase purity by X-ray diffraction technique. The powder was pressed into small pellets and sintered at various temperatures ranging from 850 – 1100°C . After checking phase purity of ceramics by X-ray diffraction technique and measuring density of the sintered samples, their microstructure was investigated using scanning electron microscopy. Roles of variables such as temperature and time in sintering process were discussed in order to find an optimum condition for fabrication of high-quality bismuth sodium zirconate ceramic.

E_E0015 MICROSTRUCTURE AND TARNISHING RESISTANCE OF SILVER-COPPER-PALLADIUM JEWELRY STERLING

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Abstract: The Ag-Cu-Pd jewelry sterling in various compositions was casted at 1025°C with the final temperature by lost-wax technique. Pd950 commercial alloy 0-1.5 wt% was used in order to determine the effect of Pd on silver sterling. The tarnish test was performed by immersing the sample in 0.1% Na₂S and 5% NaCl solutions for 1, 2, 3, 5 and 10 hours. To specify the color space from tarnishing, the surface color difference (ΔE^*) were measured by follow the Commission International d' Eclairage (CIE LAB) standard. It was found that the tarnish was improved with high Pd950 content. Microstructural investigation of the cast was studied by using an optical microscope (OM) and scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS). Dendritic phase formations were existed in all the microstructure. Secondary arms width suggested the improvement of dendrite increasing Pd950. The EDS point analysis confirmed the dissolution of Pd not only in silver matrix but also in eutectic phase which present higher Cu content than that of matrix. However, the mechanical test by Vicker microhardness at 300 g for 15 s shows no significantly difference in hardness for all the samples.