Effects of Sintering Behavior on Structure and Properties of B_2O_3 doped $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ Lead-Free Ceramics

Supalak Manotham[1], Pharatree Jaita[1,2*], Tawee Tunkasiri[1,3] and Gobwute Rujijanajul[1,3]

[1]Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

[2]Science and Technology Research Institute, Chiang Mai University, Chiang Mai 50200, Thailand

[3]Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

[*] Corresponding author. E-mail address: pharatree@gmail.com

Abstract

The effect of sintering temperature on phase structure, densification and room temperature dielectric properties of B_2O_3 doped $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$(BNBT) lead-free ceramics prepared by a solid-state mixed oxide method was investigated and presented in this work. The X-ray diffraction analysis of the ceramics suggests that all samples exhibited a single perovskite structure without any secondary phase. The coexisting of both rhombohedral and tetragonal phases was identified over the entire sintering temperature range. The optimum sintering temperature for preparation of high-density BNBT + 2 wt% B_2O_3 ceramic was found to be 1050°C. Room temperature dielectric measurement data showed that the dielectric constant and dielectric loss values were increased with increasing the sintering temperature.

Keywords: BNBT, Lead-free ceramics, Sintering, Phase, Dielectric Properties

Introduction

Piezoelectric materials are commonly used as actuators and sensors in various sensors, actuators, and micro-electromechanical devices (Maqbool et al., 2014). Lead oxide materials such as lead zirconate titanate or $Pb(Zr,Ti)O_3$ (PZT) and its solid solutions have excellent electrical properties and are most commonly used in the modern piezoelectric devices (Hussain et al., 2014). However, the waste products containing lead oxide (PbO) can cause serious human health and environment problems, making lead-free piezoelectric materials far more desirable than PZT (Acharya et al., 2014; Panda, 2009).

It is well known that bismuth sodium titanate or $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) was found to be ferroelectric with a perovskite structure at room temperature in 1960 by Smolenskii et al. (Smolensky, Isupov, Agranovskaya, & Kainik, 1961). BNT is considered as one of promising lead-free piezoelectric materials due to a large remnant polarization (P_r = 38 μC/cm^2) at room temperature and a high Curie temperature (T_c = 320 ºC). However, pure BNT ceramics is difficult to be fully poled owing to its high coercive field (E_c = 73 kV/cm), to be sintered and has relatively low piezoelectric properties (Kim et al., 2007; Chen & Hu, 2009). To improve its properties, some modifications on BNT composition have been performed. Previous studies indicate that BNT-based composition modified with $BaTiO_3$ has better piezoelectric property and easier treatment in polling process as compared with pure BNT ceramics (Gao, Huang, Hu, & Du, 2007; Takenaka, Maruyama, & Sakata, 1991; Chu, Chen, Li, & Yin, 2002; Xu, Lin, & Kwok, 2008). Among them, $BaTiO_3$ is well-known lead-free piezoelectric materials with a tetragonal

phase, and MPB (morphotropic phase boundary) compositions exist in the case of x = 0.06 – 0.07 for $(1-x)Bi_{0.5}Na_{0.5}TiO_3-xBaTiO_3$ system (abbreviated as BNBT). Moreover, the $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ exits on the rhombohedral side around the MPB region and shows fairy satisfactory electrical response (Takenaka et al., 1991).

Among, boron oxide or B_2O_3 has a low melting point of 450ºC and has been widely used as a glass additive to gain a substantial sintering temperature reduction (Liu et al., 2015). Rhim et al. (Rhim, Hong, Bak, & Kim, 2000) reported that the addition of B_2O_3 helped to improve the dielectric constant of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics. Later in 2004, Qi et al. (Qi, Chen, Wang, & Chan, 2004) reported that the dielectric properties of $BaTiO_3$ ceramics can be improved by B_2O_3 vapor addition. Jarupoom in 2010 (Jarupoom, Pengpat, & Rujijanagul, 2010) also reported that piezoelectric properties of $Ba(Zr_{0.07}Ti_{0.93})O_3$ ceramics were improved by adding B_2O_3. It was found that the ceramics added with 2 wt% B_2O_3 presented the highest piezoelectric properties.

In this work, the B_2O_3 doped on lead-free BNBT ceramics was fabricated by a solid solution method. The effect of sintering temperature on phase structure, densification and room temperature dielectric properties was investigated and discussed in details. The optimum sintering condition will be given which is expected to provide material with better electrical properties.

Experimental

The $0.94Bi_{0.5}Na_{0.5}TiO_3-0.06BaTiO_3$ powders were prepared by solid solution method. The starting materials used in this study were Na_2CO_3 (99.5%), TiO_2 (99%), $BaCO_3$ (98.5%). The raw materials were stoichiometrically weighted and mixed by ball milling for 24 h in ethanol. The dried powders were calcined in closed Al_2O_3 crucible at 800 °C for 6 h. In order to improve the densification behaviour, 2 wt% boron oxide (B_2O_3) was added into the calcined powders and then ball milling again in ethanol for 24 h. Then, the dried powder mixed with 4wt% polyvinyl alcohol (PVA) binder and pressed in to disc-shape pellets 10 mm in diameter. The green pellets were sintered at temperature ranging from 1000 °C to 1150 °C for 2 h dwell time with a heating/cooling rate of 5 °C /min in a covered alumina crucible. Phase formation of all samples was identified by X-ray diffractometer (XRD) technique. The bulk density of sintered ceramics was determined by Archimedes' method with distilled water as the media. For the electrical study, silver pasts were painted on both sides of the samples for electrical contacts. Room temperature dielectric property was determined via a LCZ-meter with frequencies ranging from 20 Hz-2000 kHz.

Results and discussion

X-ray diffraction patterns of the ceramic sintered at various temperatures are shown in Fig. 1. It can be seen that all ceramics possessed a pure pervoskite phase. B_2O_3 phase or other impurity phases were not observed for all sintering temperatures. This suggests that B_2O_3 diffused into the BNBT lattice, may be due to their very small ion size. The B^{3+} ions can act as interstitial ions in ABO_3 lattice and formed a completely homogenous solid solution.

At lower sintering temperature of 1000°C, a slight spitted peaks at 44 – 46º correspond to the rhombohedral $(1\bar{1}1)_R/(111)_R$ and tetragonal $(002)_T/$

$(200)_T$ symmetries were observed which confirmed the coexistence of both rhombohedral and tetragonal phases (Takenaka et al., 1991; Chu et al., 2002; Xu et al., 2008). With increasing sintering up to 1150°C, the coexisting of both rhombohedral and tetragonal phases was maintained but showed a domination of tetragonal over rhombohedral structure.

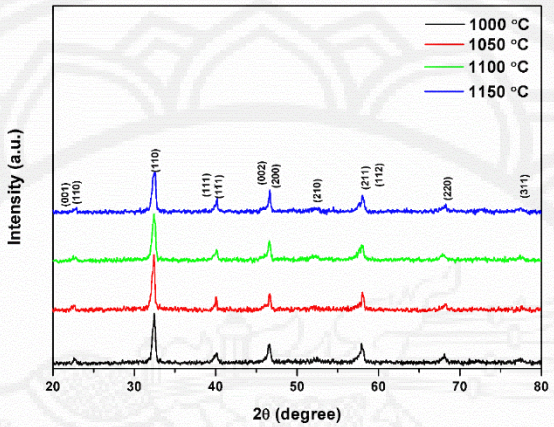

Figure 1 X-ray diffraction patterns of the ceramics sintered at various temperatures

Figure 2 presents the density and porosity values of the ceramics sintered at different sintering temperatures. The ceramic sintered at 1000 °C had a density value of 5.23 g/cm^3. The density value increased with increasing the sintering temperature and reached the maximum value of 5.56 g/cm^3 at the sintering temperature of 1050 °C and then slightly decreased at higher sintering temperature of 1100 – 1150 °C. In addition, the porosity value showed the opposite trend to that of density data. The maximum percentage of porosity value of 3.22% was obtained for the sample sintered at 1000 °C. The porosity value gradually decreased to 0.23 % with increasing the sintering temperature up to 1100 – 1150°C.

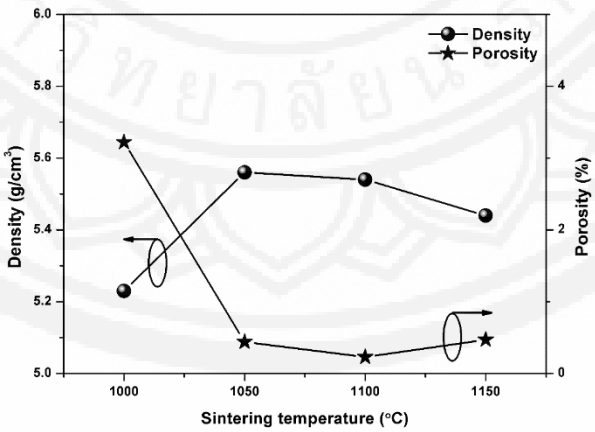

Figure 2 Plots of density and porosity values of the ceramics sintered at different sintering temperatures.

Figure 3 illustrates room temperature dielectric constant (ε_r) as a function of frequency. It can be seen that ε_r decreased with increasing frequency for all samples. The observed high values of ε_r at low frequencies may be due to the active presence of all types of polarization (i.e. atomic, ionic, dipolar and space charge polarization), however, with an increase in frequency, some of these contributions lagged behind and did not follow the field variation and became inactive. At high frequencies, all the other modes of polarization fade away and electronic polarization becomes the dominant mode of polarization, therefore, ε_r decreased at high frequencies (Moulson & Herbert, 1996). Furthermore, the dielectric constants initially increased with increasing sintering temperature and reached the maximum value of 885 (1 kHz) at the sintering temperature of 1150°C. The frequency dependence of the dielectric loss (tan δ) at various sintering temperatures is also illustrated in Fig. 4. At high frequencies the samples showed an increase in dielectric loss, especially for the high sintering samples. In addition, the dielectric loss value showed the similar trend to that of dielectric constant value. At a frequency of 1 kHz, the dielectric loss initially increased with increasing sintering temperature and reached the maximum value of 0.04 at the temperature of 1150°C.

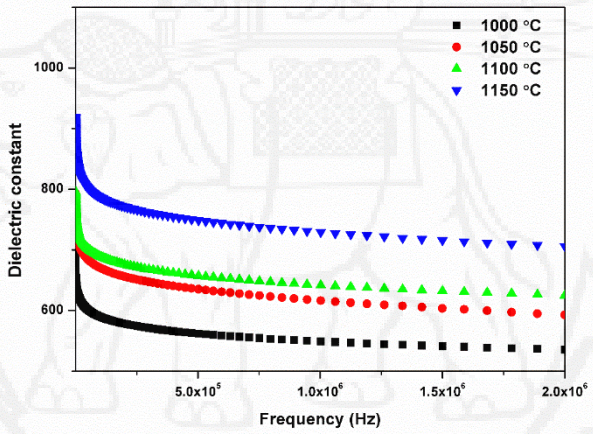

Figure 3 Room temperature dielectric constant (ε_r) as a function of frequency for the samples sintered at different sintering temperatures.

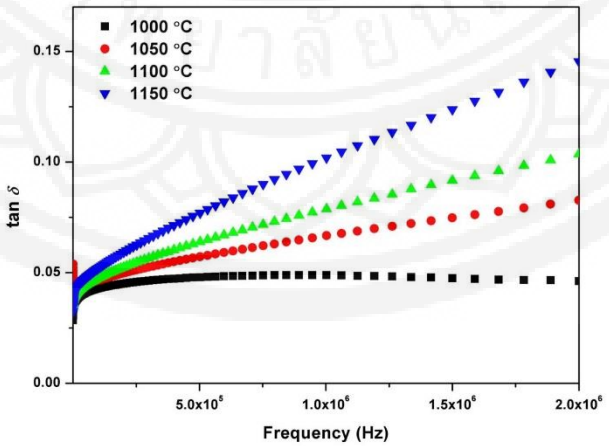

Figure 4 Room temperature dielectric loss (tanδ) as a function of frequency for the samples sintered at different sintering temperatures.

Conclusion

In this work, lead-free B_2O_3 doped $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ ceramics were successfully synthesized by a simple conventional mixed-oxide and ordinary sintering method. The ceramic samples presented a pure perovskite structure. The optimum density was noted for the sintering temperature of 1050 °C. The dielectric constant increased with an increasing sintering temperature and showed the maximum value of 885 at the sintering temperature of 1150°C.

Acknowledgments

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