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Contributed Paper

Microstructures and Mechanical Properties of Zirconium-Doped Bismuth Sodium Titanate Ceramics

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ABSTRACT

Zirconium-doped bismuth sodium titanate (BNTZ) powders were prepared using a conventional mixed-oxide method. After checking for phase purity by X-ray diffraction analysis, the synthesized powders were pressed into small pellets and sintered at high temperatures to form dense ceramics. All ceramic samples were found to be single phase with a rhombohedral structure similar to the undoped (BNT) sample. The measured densities were approximately at least 95% of their theoretical values. This observation was supported by the fact that a very small fraction of porosity was observed in the SEM micrographs of these samples. The grain sizes of Zr-doped BNT were slightly larger than that of the undoped sample. Mechanical properties of Zr-doped and undoped BNT was measured using the Knoop indentation technique. It was found that, in general, the hardness and elastic modulus of BNTZ ceramics increased with increasing zirconium content. The results suggest a way to improve the mechanical properties of BNT ceramics.

Keywords : bismuth sodium titanate, mechanical properties, microstructures, solid solution.

1. INTRODUCTION

It is well known that many solid-solution systems can produce semiconducting materials with properties that are useful for electronic and optical applications. For electroceramics, the discovery of lead zirconate titanate ($Pb(Zr,Ti)O_3$ or PZT) and its excellent piezoelectric properties has led to commercial uses of this material as transducers, actuators and sensors [1-3]. One requirement that needs to be considered when using ceramics as transducers or actuators is their mechanical properties since those ceramics must be subjected to vibration and strain. It was found for lead-based systems that by mixing antiferroelectric $PbZrO_3$ and ferroelectric $PbTiO_3$, the solid solutions of PZT with good electrical and mechanical properties could be obtained. Similar studies in non-lead ferroelectric materials such as bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$ or BNT) however have not received much interest and most of the time, only their electrical properties were measured [4-7]. From electrical measurements, BNT seems to be one of the potential lead-free ferroelectric materials that may replace lead-based compounds in the near future. Consequently, in this research, the effects of adding zirconium oxide into bismuth sodium titanate ceramics are investigated and their mechanical properties are characterized.

2. MATERIALS AND METHODS

The starting materials consisted of Bi_2O_3 (98%, Fluka), Na_2CO_3 (99.5%, Analyticals), TiO_2 (>99%, Riedel de Haën) and ZrO_2 (>99%, Riedel de Haën) powders. The stoichiometric amount of starting compounds was measured and used according to the chemical formula, $Bi_{0.5}Na_{0.5}Ti_{1-x}Zr_xO_3$, where x = 0, 0.05, 0.1, 0.15 and 0.2. Each mixture was ball-milled in ethanol for 24 h, calcined at 800 ºC for 2 hours and checked for phase purity using an X-ray diffractometer (Siemens D500). The calcined powders were then ground, sieved, and pressed into small pellets having diameter of about 15 mm in diameter and 2 mm in thickness. These pellets were sintered at 1000 ºC for 2 hours. All sintered samples were re-checked for phase purity using X-ray diffraction analysis. The measured densities of the sintered samples were approximated using the Archimedes' method. A scanning electron microscope (JEOL JSM 5910LV) was used to study the microstructure and chemical composition of these samples. A Knoop microhardness tester (Matzuwa MXTα-7) was used to study their mechanical properties.

3. RESULTS AND DISCUSSION

The X-ray diffraction analysis of the calcined powders shows that all Zr-doped samples (BNTZ) are virtually single phase and maintain the rhombohedral structure of pure BNT (Figure 1). X-ray pattern from JCPDS reference (file no. 36-0340) was also plotted for comparison. A systematic shift of peaks in the XRD pattern of BNT was most likely due to the error in zero-positioning of X-ray instrument. Nevertheless, the relative intensity and positions for X-ray peaks of the sample agreed with the reference pattern. Compared with undoped BNT sample, a slight shift of

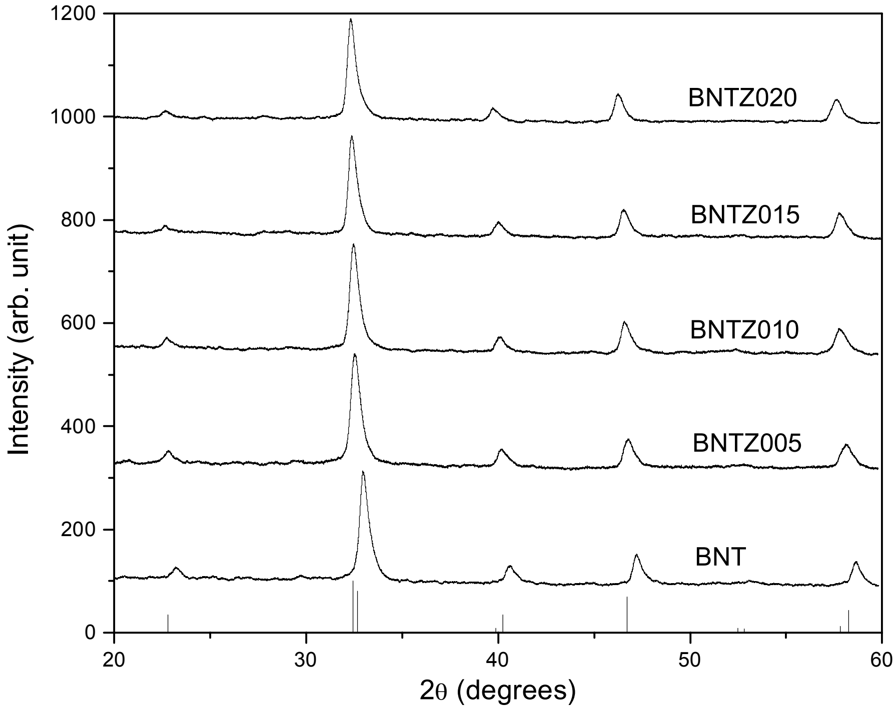

Figure 1. X-ray diffraction patterns of BNT and BNTZ powders. Note that BNT005 corresponds to BNT doped with 5 mol% Zr. JCPDS powder X-ray pattern (file no. 36-0340) was also given as a reference.

X-ray peak positions in BNTZ specimens indicates that their unit cell sizes are slightly larger than that of pure BNT. This is most likely due to the replacement of Zr ions into Ti sites and the fact that the ionic size of Zr ion is larger than that of Ti ion. Determination of small impurity peaks observed in the sample with high Zr content was rather difficult since most of the peaks were at or below the background level. By matching the peaks with JCPDS reference patterns, it is possible that the impurity belongs to a compound in Bi-Ti-O system. However, the amount present in the sample was so small that it should not have any significant effect on mechanical properties of samples under investigation.

X-ray diffraction analysis of BNTZ ceramics indicates no change in chemical composition and crystal structure from those of calcined powders. The densities of the BNTZ ceramics were measured to be in the range of 5.70-5.90 g/cm^3 and they increased with increasing amount of Zr. These values may be compared with the value of 5.87 g/cm^3 for pure BNT. All BNTZ samples had a slightly lower density than BNT except the sample with highest Zr content. Similar trend was observed in BNTZ ceramics prepared at higher sintering temperatures. SEM micrographs of BNTZ ceramics in Figure 2 shows that the grain size increases slightly as the amount of Zr increases and they all have a larger average grain size than BNT.

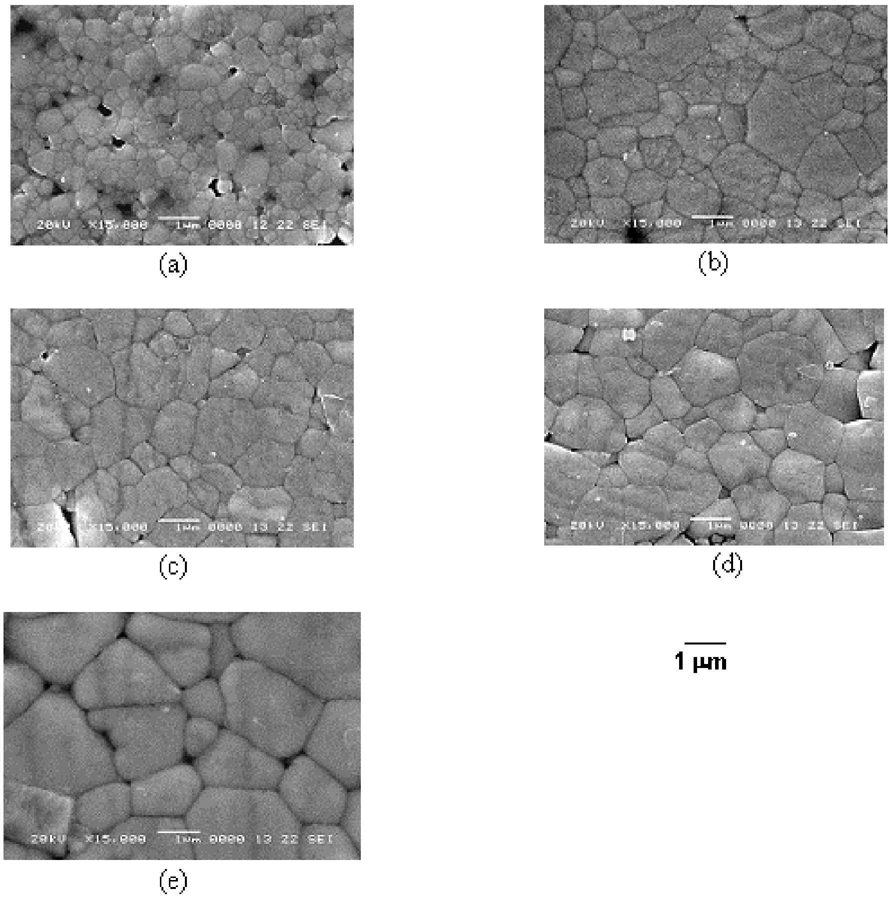

Figure 2. SEM micrographs of Zr-doped BNT ceramics with the Zr content of (a) 0 mol% (b) 5 mol% (c) 10 mol% (d) 15 mol% and (e) 20 mol%.

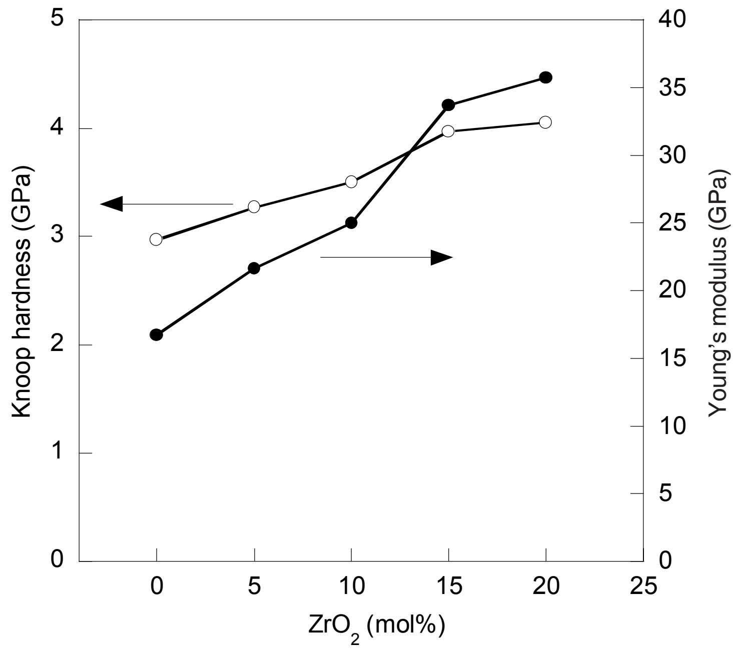

Figure 3. Knoop hardness and Young's modulus of BNT and BNTZ ceramics

Figure 3 shows the values of Knoop hardness and Young's modulus of BNTZ ceramics. The Knoop hardness of BNTZ ceramics was measured to be in the range of 3.27-4.05 GPa and it increased with increasing Zr content. These hardness values of Zr-doped BNT are slightly higher than that of undoped BNT (i.e. 2.97 GPa). The Young's modulus of BNTZ ceramics were calculated to be in the range of 21.6-35.7 GPa. These values are higher than the value of 16.7 GPa in pure BNT. There are two main factors that can cause this type of observed mechanical properties i.e. Zr concentration and microstructure of the ceramics. Although it has been known that pure metals can be hardended by addition of solute atoms, there is not much information on the effects of solid solution on mechanical properties of ceramics. It is possible that in this case the variation of ionic size in the lattice could moderately inhibit the deformation caused by the hardness indentor and resulted in an increase in hardness and elastic modulus with increasing Zr content. From microstructural aspect, the differences in density and grain size of BNT and BNTZ ceramics were quite small and these were expected not to play a significant role in determining the mechanical properties. The grain size independence of hardness was also reported in the case of PLZT ceramics [8]. In this investigation, it seems that by doping BNT with zirconium, the mechanical properties of the ceramics can be improved.

4. Conclusions

The bismuth sodium titanate zirconate solid-solution ceramics have been successfully prepared and characterized. The results from X-ray diffraction data showed that all samples were virtually single phase. A slight shift of X-ray peaks when ZrO_2 were added into BNT compound suggests that larger Zr ions occupied Ti sites. From SEM micrographs and measured density, all ceramic samples investigated were very dense. The grain size of Zr-doped BNT specimens were found to be slightly larger than those of undoped BNT. The Knoop hardness and Young's modulus were found to increase with increasing Zr content. This seems to suggest a way to improve mechanical properties of BNT compound.

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