



International Journal of ChemTech Research CODEN(USA): IJCRGG ISSN : 0974-4290 Vol. 3, No.1, pp 488-494, Jan-Mar 2011

Synthesis and Characterization of CeO₂ doped Bismuth sodium potassium titanate Ceramics

S. Supriya, S. Kalainathan and S. Swaroop*

School of Advanced Sciences, VIT University, Vellore-14. India

*Corres.author: sathyaswaroop.n.r@gmail.com Tel: +91 416 2202350 Fax : +91 416 2240411

Abstract: Pure and cerium dioxide doped bismuth sodium potassium titanate (CeO₂ doped BNKT) ceramics were synthesized by conventional method. CeO2 doped BNKT was prepared according to the composition $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_{3x} CeO_2$ where x = 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 wt %. The heat treated powders were calcined from 800 to 900 °C for 2 h. The samples were sintered from 1000 to 1100 °C for 1 hr. The phase formation was confirmed by X-ray diffraction (XRD). The microstructures of the samples were analyzed by scanning electron microscope (SEM). It was observed that the there was a decrease in grain size with the increase in CeO₂. Further, square pillar morphology was observed in the microstructures. The fourier transform infrared spectroscopy (FTIR) was used to investigate the phase evolution of compounds. The particle size measurement done for the sample (1 wt % CeO₂ doped BNKT) using laser scattering particle size distribution analyzer revealed a particle size around 592 µm.

Key words: Sintering; Thermal; Scanning electron microscopy; X-ray analysis.

INTRODUCTION

Bismuth sodium titanate Bi_{0.5}Na_{0.5}TiO₃ (BNT) is a perovskite ABO₃ type ferroelectric material discovered by Smolenski et al. in 1960 [1]. Compared to lead oxide based piezoelectric ceramics, BNT is considered to be an excellent non-lead based material due to its strong ferroelectric property with large remnant polarization. BNT shows anomalous dielectric transition from antiferroelectric to ferroelectric state around 200 °C. But this material has a drawback of high conductivity and high coercive field which are disadvantageous in the poling process. Moreover, because of the absence of lead, these are non-toxic [2]. To improve the electrical properties of bismuth titanate based compounds such as Bi_{0.5}K_{0.5}TiO₃ (BKT) and BNT with various dopants such as SC₂O₃, La₂O₃ and Dy₂O₃ have been investigated in the literature. Similarly, it was shown that the electrical properties of bismuth titanate compounds can be improved by adding BaTiO₃ [3], NaNbO₃ [4], BiFeO₃ [5], La₂O₃ [6], and WO₃ [7]. They showed improved piezoelectric and easy poling properties. Other than these materials,

potassium bismuth sodium titanate (Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO₃ or BNKT) currently widely investigated as it is also a lead free ferroelectric material [14]. It shows improved piezoelectricity and maximum remnant polarization [8-12]. It has rhombohedral structure with low dielectric constant and high piezoelectric constant with good electromechanical coupling factor [13].

In addition, BNKT has been investigated in terms of various dopants and the formation of solid solutions with other compounds. For example, cerium dioxide doping in Bi0.5Na0.44K0.06TiO3 material has been reported to cause improvements in electrical properties at different temperatures [14]. However, a detailed microstructural investigation comparing pure and CeO_2 doped BNKT has not been done so far.

As far the microstructural analysis in other related compounds, Yi et al. have reported that the grain growth was much more effective when La³⁺ ions was added to BNT ceramics [15]. Similarly, Watcharapasorn et al. investigated the grain growth behavior of BNT ceramics with dysprosium doping.

489

They studied the effect of dopant substitution on grain morphology [16]. In this paper we present the microstructure and particle size measurement of the systems of $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ with different levels of CeO₂ doping, which is not reported in the literature so far.

EXPERIMENTAL PROCEDURE

The Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO₃ + x wt % CeO₂ (x = 0 to 1.0) ceramics were prepared by conventional methods. Analytical grade reagents with 99 % purity of Bi₂O₃, Na₂CO₃, K₂CO₃, and TiO₂ (Sigma aldrich) were used as raw materials. According to the composition of Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO₃ + x wt % CeO₂ (x = 0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0), the appropriate amount of raw materials were weighed according to the stoichiometric ratio. The weighed powders were wet grounded in planetary mill with agate mortar in ethanol for 2 hours. After drying, the powders were calcined at 800 - 900 °C for 2 hrs. The calcined powders were reground by planetary mill with agate mortar and ethanol for 2 hrs. The dried powders were sintered from 1000 to 1100°C for 1 hr in air.

X-ray powder diffraction (XRD) patterns were taken with Philips-PW3040/60, X'pert PRO Analytical Xray diffractometer with CuK α radiation ($\lambda = 1.5418$ Å) and graphite monochromator. The diffraction data was recorded for 2 θ values between 10 and 80° with a step size of 0.02°. The microstructure of sintered samples was observed with scanning electron microscope (JSM-5610LV). The FT-IR spectrum of the specimens was measured by a Jasco FT-IR-300E spectrometer using KBr method in the wave number range of 400– 4000 cm⁻¹. By using laser scattering particle size distribution analyzer (Horiba LA-910) the particle size measurements were carried out.

RESULTS AND DISCUSSION





Figure 1 shows the powder XRD patterns of pure and CeO_2 doped BNKT powders. The X-ray diffraction pattern indicates the formation of perovskite type structure in solid solutions. The lattice distortion occurred between 30 to 50° implying that CeO_2 diffused into the BNKT ceramics [17]. The (hkl) of the reflecting planes of the CeO_2 doped BNKT were two peaks corresponding to (003) at about 39.8° and other peak corresponding to (202) at around 47° indicating the rhombohedral symmetry structure. Because the addition of CeO_2 does not show any obvious change in the phase structure, the rhombohedral structure remains same for all levels of CeO_2 doping [17]. The scanning electron micrograph (SEM) images of pure BNKT and CeO_2 doped

BNKT of x = 0.1, 1.0 samples have been shown in Figure 2, 3 and 4 respectively. The microstructure of these three samples has been observed. Due of doping of CeO₂ in BNKT there was a decrease in grain size.

Figure 2. SEM micrograph of pure BNKT



Figure 3. SEM micrograph of x = 0.1 %wt of CeO2 doped BNKT





Figure 4. SEM micrograph of x = 1.0% wt of CeO2 doped BNKT

Figure 5. FTIR spectra of pure BNKT







Figure 6. FTIR spectra of x = 0.1 %wt CeO2 doped BNKT



Figure 7. FTIR spectra of x =1.0 %wt CeO2 doped BNKT



Figure 5, 6 and 7 shows fourier transform infrared spectroscopy (FTIR) of pure BNKT, x = 0.1 and 1.0 wt % doped BNKT powders respectively. From figure 5, the band at 629.96 cm⁻¹ confirms the formation of BNKT compound. The bands at 1386.41, 1627.51, 2391.15 and 3441.15 cm⁻¹ confirm the octahedral BO_6 groups in perovskite structure proving B-O bonds along c-axis and confirm the presence of oxide groups. From figure 6, the band at 438.13 cm^{-1} confirms the presence of x = 0.1 wt % doped CeO₂ in BNKT compound. The band at 615.5 cm⁻¹ confirms the presence of BNKT compound and the bands at 1383.93, 1625.80, 2340.63 and 3488.01 cm⁻¹ confirm the presence of oxide groups and B-O bonds. From figure 7 the band at 436.77 cm⁻¹ confirms the presence x = 1.0 wt % doped CeO₂ in BNKT compound. The band at 612.77 cm⁻¹ confirms the presence of BNKT compound. The bands at 1624.21, 2379.64, 3455.95 cm⁻¹ confirms the presence of oxide groups.

Figure 8 shows the variation of particle size with frequency and particle size with cumulative percentage for $x = 1.0 \text{ CeO}_2$ doped BNKT powders. Table 1 shows data of particle sizes with different frequency levels. At maximum frequency level of 31.2 % the particle size has been determined around 592.4 µm.

CONCLUSION

In this study pure BNKT and x = 0.1 to 1.0 wt % doped CeO₂- BNKT ceramics were prepared by conventional ceramic technique. The phase formation has been confirmed by X-ray diffraction analysis. The changes in grain sizes according to the various levels of dopant of CeO₂ in BNKT have been studied by using scanning electron micrograph. The SEM images show the square pillar shaped morphology of the compound. The FTIR spectrum analysis has been done to confirm the presence of functional groups of pure and doped BNKT powders. The particle size measurement data for different frequency levels has been done by using particle size distribution analyzer.



Figure 8. Particle sizes of x = 1.0 % wt CeO2 doped BNKT powder

Table 1. Particle sizes of x = 1.0 %wt CeO2 doped BNKT powder with frequency measurement

Size(µm)	Frequency (%)	Und(%)
1019.5	0.35	100.00
890.1	2.89	99.65
777.1	9.50	96.75
678.5	20.61	87.25
592.4	31.21	66.64
517.2	13.14	35.43
451.6	1.28	22.29
394.2	0.12	21.01
344.2	0.00	20.89
300.5	0.00	20.89
262.4	0.20	20.89
229.1	0.27	20.69
200.0	0.22	20.42
174.6	, 0.00	20.20
152.5	0.00	20.20
133.1	0.00	20.20
116.2	0.00	20.20
101.5	0.00	20.20
88.58	0.15	20.20
(7.54	0.42	20.06
07.32	0.72	19.03
51.47	0.82	18.92
21.47	0.82	17.09
20.22	0.02	16.66
39.23	0.45	15.00
29.91	0.21	15.90
20.11	0.13	15.09
19.00	0.12	15.54
17.38	0.11	15.42
15.17	+ 0.10	15.21
13.25	0.11	15.10
11.56	0.11	14.00
10.10	0.12	14.99
10.10	0.15	14.80
8.810	0.19	14.72
(.720	0.25	14.55
0.720	0.35	14.27
5.867	0.45	13.92
5.122	0.57	13.4/
4.472	0.69	12.90
3.905	0.81	12.21
3.409	0.79	11.40
2.976	0.75	10.61
2.599	0.69	9.85
2.269	0.54	9.17
1.981	0.42	8.62
1.729	0.32	8.20
1.510	0.23	7.88
1.318	0.16	7.65
1.151	0.11	7.49
1.005	0.00	7.38
0.877	0.00	7.38
0.766	0.00	7.38
0.058	0.44	0.44
0.022	0.00	0.00

ACKNOWLEDGEMENTS

Authors are thankful to Dr. R. Jagdheesh for recording of SEM image and the management of VIT University, Vellore for their constant financial support.

REFERENCES

1. Wang X.X., Kwok K.W., Tang X.G., Chan H.L.W., Choy C.L., Electromechanical properties and dielectric behavior of $(Bi_{1/2}Na_{1/2})_{(1-1.5x)}Bi_xTiO_3$ lead-free piezoelectric ceramics, Solid State Commun., 2004,129,319-323.

2. Chan H.L.W., Choy S.H., Chong C.P., Li H.L., Liu P.C.K., Bismuth sodium titanate based lead-free ultrasonic transducer for microelectronics wire bonding applications, Ceramics Int., 2008, 34,773-777.

3. Hwi-Yeol P., Cheol-Woo A., Hyun-Cheol S., Jong-Heun L. and Sahn N., Microstructure and piezoelectric properties of $0.95(Na_{0.5}K_{0.5})NbO_3$ -0.05BaTiO₃ ceramics, Applied physics lett., 2006, 89,96-99.

4. Yue-Ming L., Wen C., Jing Z., Qing X., Xing-Yong G., Run-Hua L., Impedance spectroscopy and dielectric properties of $Na_{0.5}Bi_{0.5}TiO_3$ -NaNbO₃ ceramics, Physica B: Condensed Matt., 2005, 365,76-81.

5. Changrong Z., Xinyu L., Weizhou L., Changlai Y., Structure and piezoelectric properties of $Bi_{0.5}Na_{0.5}TiO_3$ - $Bi_{0.5}K_{0.5}TiO_3$ - $BiFeO_3$ lead-free piezoelectric ceramics, Materials Chemistry and Phy., 2009, 114,832-836.

6. Feng Q., Jun-Hui H., Jun Z., Xiao-Bing C., Ferroelctric and dielectric properties of bismuth layered structural $Sr_2Bi_{4-x}Ln_xTi_5O_{18}$ (Ln = La, Nd, Sm and Dy) ceramics, J. of Solid State Chem., 2006, 179,1768-1774.

7. Prasad K., Kumari K., Lily., Chandra KP., Yadav KL., Sen S., Glass-like response of (Na_{1/2}Bi_{1/2})TiO₃–WO₃ ceramic, Solid State Commun., 2007, 144,42-45.

8. Raghavender M., Kumar G.S., Prasad G, Modification of dielectric relaxations in sodium bismuth titanate with samarium doping, J. of Phy. and Chem. of Sol., 2006, 67,803-808.

9. Bahuguna Saradhi B.V., Srinivas K., Prasad G., Suryanarayana S.V., Bhimasankaram T., Impedance spectroscopic studies in ferroelectric $(Na_{1/2}Bi_{1/2})TiO_3$, Mat. Sci. and Engg B., 2003, 98,10-16.

10. Yueming L., Wen C., Qing X., Jing Z., Xingyong G., Piezoelectric and ferroelectric properties of $Na_{0.5}Bi_{0.5}TiO_3-K_{0.5}Bi_{0.5}TiO_3-BaTiO_3$ piezoelectric ceramics, Materials Lett., 2005, 59,1361-1364.

11. Changrong Z., Xinyu L., Weizhou L., Dielectric and piezoelectric properties of BiFeO₃ modified Bi_{0.5}Na_{0.5}TiO₃–Bi_{0.5}K_{0.5}TiO₃ lead-free piezoelectric ceramics, Mat. Sci. and Engg. B., 2008, 153,31-35.

12. Hussain A., Ahn C.W., Lee H.J., Kim I.W., Lee J.S., Jeong S.J., Rout S.K., anisotropic electrical properties of $Bi_{0.5}(Na_{0.75}K_{0.25})_{0.5}TiO_3$ ceramics fabricated by reactive templated grain growth (RTGG), Current Applied Phy., 2009,10,305-310.

13. Kresel J., An x-ray diffraction and Raman spectroscopy investigation of A-site substituted perovskite compounds: the $(Na_{1.x}K_x)_{0.5}Bi_{0.5}TiO_3$ (0<x<1 solid solution, J.Phys: Condensed mat., 2000, 12,3267-3280.

14. Yueming L., Wen C., Qing X., Jing Z., Yan W., Huajun S., Piezoelectric and dielectric properties of CeO₂-doped Bi_{0.5}Na_{0.44}K_{0.06}TiO₃ lead-free ceramics, Ceramics Inter., 2007, 33,95-99.

15. Jiang X.P., Lin L.Z., Eng M.Z., Chan H.L.W., Dielectric properties of Mn-doped $(Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO_3$ ceramics, Material lett., 2006, 60,1786-1790.

16. Yi J.Y., Lee J.K., Hong K.S., Dependence of the microstructure and the electrical properties of lanthanum – substituted $(Na_{1/2}Bi_{1/2})TiO_3$ on cation vacancies, J. Am. Ceram. Soc., 2002, 85,3004-3010.

17. Watcharapasorn A., Jiansirisomboon S., Grain growth kinetics in Dy-doped $Bi_{0.5}Na_{0.5}TiO_3$ ceramics, Ceramics Inter., 2008, 34,769-772.
