SYNTHESIS AND MICROSTRUCTURES STYDY OF ANTIMONY AND NICKEL-DOPED BISMUTH SODIUM TITANATE ZIRCONATE CERMICS

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ABSTRCT

$(Na_{0.5}, Bi_{0.5})(Ti_{0,8}\ Zr_{0,2})_{1-x}(Sb_{2/3}, Ni_{1/3})_xO_3$ (NBTZSN) ceramics with x= 0.05 and 0.1 were synthesized using a high-temperature solid-state reaction technique. X-ray diffraction (XRD) technique, FTIR and scanning electron microscopy (SEM) were used to study the structural and microstructural properties of the compounds, respectively. The XRD study confirmed the formation of a single-phase polycrystalline compound with tetragonal crystal structure and minority of pyrochlore phase at room temperature. Microstructural analysis of the surface of the compounds exhibits that there is a change in grain size, shape and density on introduction of (Sb) and (Ni) in (NBTZ).

KEYWORDS: NBTZ, DRX, Perovskite:, Pyrochlore phase.

RESUME

Les céramiques $(Na_{0.5}, Bi_{0.5})\ (Ti_{0,8}\ Zr_{0,2})_{\ 1-x}\ (Sb_{2\ /\ 3},\ Ni_{1\ /\ 3})_{\ x}O_3$ (NBTZSN) avec x = 0.05 et 0.1 ont été synthétisées en utilisant une réaction à l'état solide à haute température technique. La technique de diffraction des rayons X (XRD), le FTIR et la microscopie électronique à balayage (SEM) ont été utilisés pour étudier les propriétés structurelles des composés, respectivement. L'étude XRD a confirmé la formation d'un composé polycristallin monophasé avec une structure cristalline tétragonale et une minorité de phase pyrochlore à température ambiante. L'analyse microstructurelle de la surface des composés montre qu'il y a un changement dans la taille et la densité des grains lors de l'introduction de (Sb) et (Ni) dans (NBTZ).

MOTS-CLÉS: NBTZ, DRX, Perovskite:, Phase pyrochlore.

1 INTRODUCTION

Since the discovery of ferroelectric phenomena in perovskit $BaTiO_3$ (BT) in 1940s [1], a large number of oxides of different structural families were examined to get the behavior of the materials. Among all the ferroelectric oxides studied so far, some perovskite oxides were found to be useful for some solid state electronic devices such as random access memory devices, high dielectric constant capacitor, pyro-electric detectors, imaging devices, electrooptic devices, modulators etc. [2, 3]. Among the studied ferroelectric oxides, some lead based ferroelectric oxides such as lead titanate, lead zirconium titanate etc. are found to be most suitable for fabrication of various solid state devices. Unfortunately, because of the toxic nature they produce environmental pollutions [4, 12]. Therefore, attempts are now being made to search lead free new ferroelectric materials which can be a replacement of lead based ferroelectrics without losing much of their physical properties required for devices. $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is one of such lead free ferroelectric materials [5]. However, there are some problems of NBT such as high dielectric loss, high conductivity, low depolarization temperature (Td) and high coercive field (73 kV/cm) which limits the material to be used for devices. There are various ways to solve these problems and enhance electrical properties. One of the

possible ways to solve the above problems is by making solid-solutions of two similar types of perovskites (near morphotropic phase boundaries) or modifying the base compound with suitable substitutions. Also, numerous amount of works are still going on to modify NBT by suitable substitutions at the A and /or B sites of perovskite. Zhang et al [6,7] studied the substitution of zinc in NBT results in decreased Td and enhanced relaxor behavior. The piezoelectric constant of Zr modified NBT was studied by Watcharapasorn and Jiansirisomboon [8] and it reduced with increasing of Zr concentration. Consequently, in this research, the effects of adding antimony and nickel oxide into bismuth sodium titanate zirconate (NBTZ) ceramics are investigated and their microstructures are characterized.

2 EXPERIMENTAL PROCEDURES

$(Na_{0.5}\ Bi_{0.5})(Ti0_{,8}\ Zr_{0,2})_{1-x}(Sb_{2/3}\ ,Ni_{1/3})_xO_3$ (BNTZSN) polycrystalline ceramic powders with x= 0.05 and 0.1were prepared by a mixed oxide method at high temperatures using high purity oxides: Bi_2O_3 (98), Na_2CO_3 (99.5), NiO (99.4), Sb_2O_3 (99.5), TiO_2 (>99%) and ZrO_2 (>99%,) in a suitable stoichiometry. The oxides were mixed thoroughly in aceton medium using magnetic stirrer for 24 h. medium using glass mortar. The obtained paste was dried at 75 °C, and then crushed in a glass mortar for 4 hours. The mixed oxides were, first, fired (calcined) at 850 °C for about 4 h at a heating rate of 2 °C/min. The calcined powders were crushed in a similar manner to the first crushing but for 5 hours, for better size reduction. A 5 % polyvinyl alcohol (PVA) water solution was used as a binder to increase the plasticity of the powders [8]. The weight ratio of the PVA solution and the powders was 1: 20. The powder and PVA solution were mixed in a mortar and then uniaxially pressed into pellets at a pressure of 200 MPa in a cylindrical stainless steel die using a hydraulic press. The size of those pellets was 13 mm in diameter; while their thickness was 2 mm. These pellets were then sintered conventionally at three different temperatures, 1000, 1150 and 1200 °C and for 4 h. The formation and quality of the desired compounds were checked by X-ray diffraction (XRD) technique with powder diffractometer (BRUKER-AXE, D8) using CuK radiation (l =1.5406 Å) at room temperature and FTIR analys. The measured densities of the sintered samples were approximated using the Archimedes method, the maximum value of the density corespond to the temperature 1200 °C . The microstructures of the samples were analysed by scanning electron microscopy (SEM) (JEOL JSM 5910LV) figure 1.

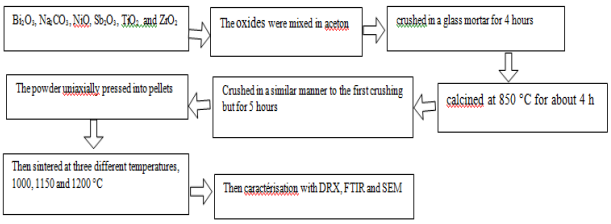

Figure 01: Experimental set-up

3 RESULTS AND DISCUSSION

2.1 Structural Studies

X-ray diffraction patterns of NBZTSN ceramics sintered at 1200°C are shown in "Figure 2". The observed X-ray diffraction peaks are sharp and single, and they are different from the patterns of the ingredients. This confirms the good homogeneity and crystallization of the prepared sample. The XRD data have been analyzed by comparing with the JCPDS Card No. 01- 070- 4760- for all ceramics. All the peaks in the XRD pattern of the samples were indexed in tetragonal crystal system using a computer program 'Highscor' [9]. However, there is an additional peak near the (020) usually referred as secondary or pyrochlore phase [10]. This undesired phase, i.e. pyrochlore phase with poor electrical properties due to large defect density as a result of oxygen deficiency [8], with general formula $Bi_4Ti_3O_{12}$ and JCPDS Card No 01-089-7503. .

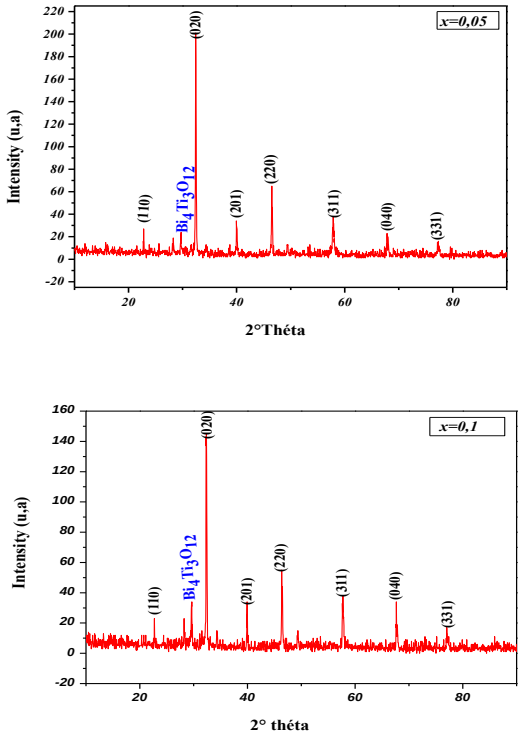

Figure 02: X-ray diffraction pattern of NBTZSN calcined at 1200 C°

All the lattice parameters of the compounds were calculated using a powder diffraction refinement computer program (celref) and the crystal structure is found to be tetragonal with space group p4bm. The lattice parameters and unit cell volume, of the materials are presented in Table 1. The particle size of modified NBTZ increases with increase in (Sb, Ni) content (Table 1).

Table 01: Comparison of lattice parameters (a and c) and unitcell volume (V) of modified NBTZ

Concentration x	a=b (Å)	c (Å)		V(A^3)

			$\alpha = \beta = \gamma(^\circ)$	
0.05	**5.5139**	**3.9233**	**90**	**119.28**
0.1	**5.5287**	**3.9131**	**90**	**116.26**

2.2 Microstructural Studies

2.2.1 Scanning electron microscopy

Figure 3. shows the scanning electron micrograph (SEM) of sintered $(Bi_{0.5}Na_{0.5}(Ti_{0,8}\ Zr_{0,2})_{1-x}(Sb_{2/3}\ ,Ni_{1/3})_xO_3$) ceramics. The micrographs indicate that the inhomogeneous distribution of polycrystalline grain throughout the surface of material. The average grain size calculated from the micrograph of NBTZSN is between 13.58 µm and 15.77 µm. On the other hand, the secondary pyrochlore phase is clearly present on the micrographs as cubic particulates [15,16] which agrees well with the secondary peak observed in XRD (Fig.1).

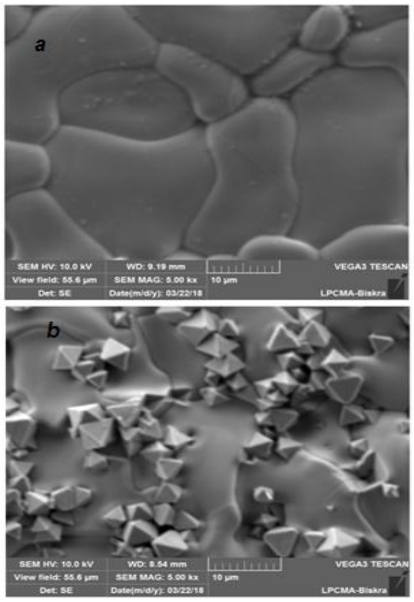

Figure 03: SEM micrograph of NBTZSN powders with the (Sb, Ni) content of (a) 5 mol% (b) 10 mol% calcined at 1200 C°

4 FOURIER TRANSFORMED INFRARED STUDIES

Figure.4 shows the FTIR spectrum of the sintered powders, a peak is observed with absorption band at 3444.6 $cm^{-1}(\upsilon_1)$ may be assigned to the stretching of –OH groups present in water [13] and there were two other distinct absorption bands at 597 cm^{-1} (υ_2), 536 cm^{-1} (υ_3) observed. These absorption bands resemble with the reported FTIR observations of PZT ceramics. In the perovskite structures the TiO6 octahedral is responsible for two distinct vibration modes: one at 563 cm^{-1} attributed to bending vibration and another at 597 cm^{-1} due to stretching of octahedral [10,11]. The absorption bands υ_3 represent bending modes while υ_2 represent stretching modes in the BO_6 octahedron in ABO_3 structure Figure5.

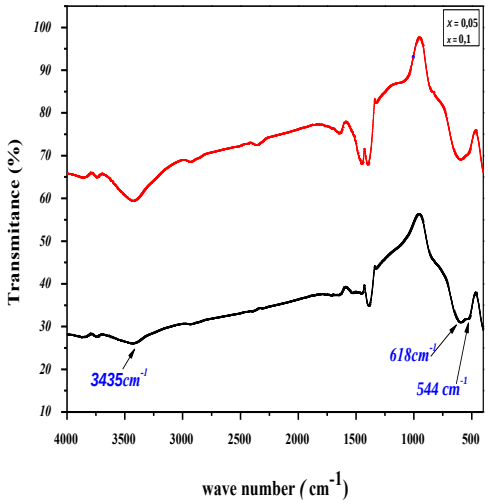

Figure 04: FTIR spectra of NBTZSN Powders calcined at 1200 C°

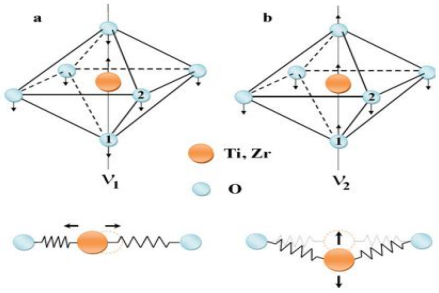

Figure 05: Schematic infrared active normal vibrations of a TiO_6 octahedron, (a) higher frequency stretching vibration and (b) lower frequency bending vibration

5 CONCLUSION

The (Sb, Ni) modified NBTZ polycrystalline powders were synthesized by a high-temperature solid-state reaction technique. The formation of the materials was confirmed by preliminary X-ray diffraction analysis. The (Sb, Ni) modified NBTZ samples have tetragonal crystal system with minority of pyrochlore phase. The grain size of the samples was found to be decreased on (Sb, Ni) substitution in NBTZ, The optical properties of the NBTZSN were investigated by transmittance measurements, two bands were observed from the FTIR graphs, the first one represent bending modes while the second represent stretching modes in the BO_6 (TiO_3 and ZrO_3).

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