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The effects of sintering temperature and titanium ratio on structural and electrical properties of new PZT-CNS ceramics

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ABSTRACT

In this contribution, (0.80-x)Pb($Cr_{1/5}$,$Ni_{1/5}$,$Sb_{3/5}$)O_3-x$PbTiO_3$-0.20$PbZrO_3$ perovskite ceramics namely PZT-CNS were prepared by solid state reaction method. The obtained samples have been characterized by different techniques including XRD, density test, SEM analysis, and Dielectric measurements in order to investigate the effects of sintering temperature and titanium content on microstructure and dielectric properties. The obtained experimental results have been reported and well discussed.

1. INTRODUCTION

Ceramic materials type perovskite ABO_3 have received extensive attention due to their attractive physical and chemical features including electronic conductivity, electrically active structure, thermal and chemical stability, photocatalytic, thermoelectric, and dielectric properties. These ceramics are widely used in catalysis, fuel cells, and electrochemical sensing [1]. Lead zirconate titanate (PZT) based ceramic materials have been largely used for piezoelectric applications due to their excellent potential properties especially at the morphotropic phase boundary (MPB). These kind of engineering materials can find an application in the fabrication of capacitors, sensors, actuators, and other high piezoelectric devices [2–8].

Doping pure PZT by using different chemical elements has excited a great interest from both industry and academia [9]. The studies based on PZT ceramics have demonstrated that substitution in both cationic and anionic sites can improve their properties [10]. In a study, it was found that the dielectric properties of PZT were improved after strontium Sr^{2+} incorporation in A site [11]. In other study, it was revealed that the substitution of Pb^{2+} by La^{3+} in PZT ceramics leads to improve both dielectric constant and Curie temperature [12]. S.Y. Chu et al. have reported an increase in piezoelectric and dielectric properties of PZT ceramics after Nb^{5+} addition in site B [13]. Abba and coworkers have observed an improvement in piezoelectric properties of PZT ceramics after the insertion of La^{3+} and Mo^{6+} in A and B simultaneously [14].

Pure and doped PZT ceramics can be easily elaborated by solid state reaction method. In this technique, different weight proportions of the oxides entering in the composition of the required phase are mixed in solvent usually acetone, the final mixture are calcined and milled to obtain the desired PZT phase [15].

To best of our knowledge, there is no experimental background has been proposed to study the effects of sintering temperature and titanium molar ratio on the properties (0.80-x)Pb($Cr_{1/5}$,$Ni_{1/5}$,$Sb_{3/5}$)O_3-x$PbTiO_3$-0.20$PbZrO_3$. The aim of the present work is to elaborate series of PZT-CNS ceramics and to investigate the effects of sintering temperature and titanium content on microstructural and dielectric properties of prepared samples of PZT-CNS ceramics.

2. EXPERIMENTAL PART

2.1 Samples preparation

PZT-CNS ceramic samples have been prepared using solid state reaction process. Stoichiometric amounts of highly pure Pb_3O_4 (99.9 % purity, Aldrich chemicals), ZrO_2 (99.90 % purity, Biochem), TiO_2 (99.9 % purity, Biochem), Cr_2O_3 (99.6 % purity, Alfa Aesar), Sb_2O_3 (99.90 % purity, Biochem), and NiO (99.6 % purity, Alfa Aesar) were used as starting reagents to prepare (0.80-x)Pb($Cr_{1/5}$,$Ni_{1/5}$,$Sb_{3/5}$)O_3-x$PbTiO_3$-0.20$PbZrO_3$ oxides with $0.30 \leq x \leq 0.42$. The mass proportions of different oxides powders entering in each ceramic composition were mixed in acetone medium for 24 h using a magnetic stirrer and then dried in oven at 80 °C. The resulting mixture was milled for 6 hours and calcined at 900 ˚C for 2h. The calcined powders were milled again and sintered at 1180 °C for 2h to obtain pellets of 2 mm thickness used to perform XRD, SEM analysis, density test, and dielectric measurements.

2.2 Structural characterization

PZT-CNS powders have been the subject of X-ray diffraction test using Bruker Advanced D8 diffractometer, Cu-Kα1=1.5406 Å, scans were recorded in the range of 2θ varies from 10 to 90˚ at a scanning rate of 2˚/min.

2.3 SEM analysis

Pellets of PZT-CNS have been examined by SEM analysis

using JEOL JSM-6390LV machine to study microstructure of the elaborated samples.

2.4 Density measurements

Sintered pellets of cylindrical form as show in figure 1 were used to measure density by the relation (1) [16]:

$$D = \frac{m}{V} = 1{,}2733\frac{m}{D^2.e} \quad (1)$$

The porosity of the studied pellets is given by following equation 16:

$$P = 1 - \frac{D}{D_{theo}} \quad (2)$$

where:
m: mass of pellet,
D: diameter of pellet,
e: thickness of pellet,
V: volume of pellet.

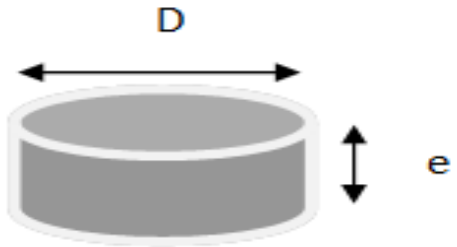

Figure 1. Form of pellet used for density test

2.5 Dielectric measurements

Sintered pellets of the samples with different compositions were polished and silver pasted in both sides to make ohmic contacts. Dielectric measurement was carried out using LCR meter (Good Will Instrument Co., LTD) operating in the frequency range 1-200 KHz. The dielectric constant ε was calculated from the capacitance at a frequency of 1 KHz following the relation [15]:

$$\varepsilon' = \frac{C}{C_0} = \frac{C.e}{\varepsilon_0.S} \quad (3)$$

In equation (3), C is the measured capacitance of the studied pellet, C_0 is the capacitance of an empty capacitor, e is the pellet thickness in mm, S is pellet surface in mm^2 and ε_0 is the permittivity of free space charge ($\varepsilon_0 = 8.85 \times 10^{-14}$ F/cm). In the other hand, loss tan is calculated using the equation [15]:

$$tg\delta = R.C.W \quad (4)$$

where:
R: electrical resistance of tested pellet in Ohm
C: the capacitance of tested pellet in F.
W: pulsation in Hz.

3. RESULTS AND DISCUSSIONS

3.1 XRD results

XRD analysis is used for the phase identification of the elaborated powders sintered at 1180. XRD patterns corresponding to samples with molar ratio (20/30/50, 20/33/47, 20/36/44, 20/39/41; and 20/42/38) are shown in Figure 2.

XRD data of the samples under investigation were compared with JCPDS database. It was found that the samples under probe exhibit a pure perovskite phase of tetragonal structure and no secondary phase has been detected, indicating that Cr, Ni and Sb are totally diffused into PZT lattice to form the PZT-CNS solid solution.

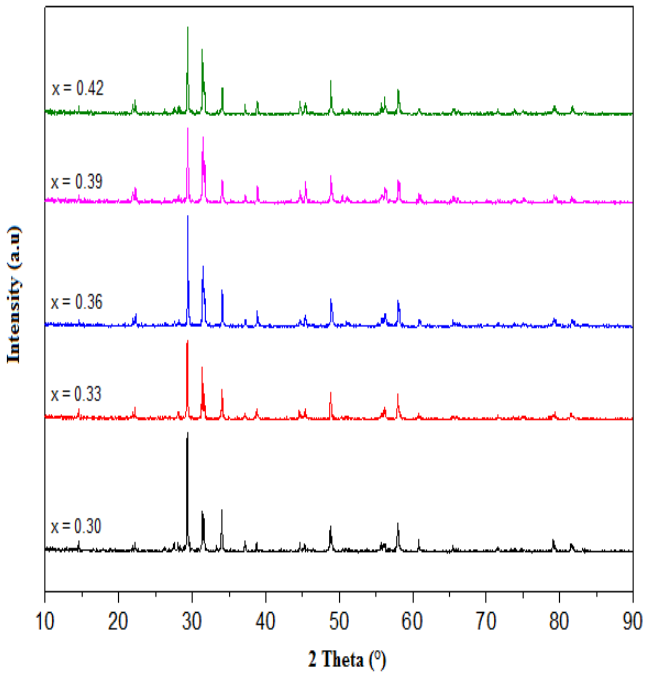

Figure 2. X-ray diffraction patterns of (0.80-x)Pb($Cr_{1/5}$,$Ni_{1/5}$,$Sb_{3/5}$)O_3-x$PbTiO_3$-0.20$PbZrO_3$ ceramics sintered at 1180 °C for 2 h with $0.30 \leq x \leq 0.42$

Structure refinement of the obtained PZT-CNS ceramics has been realised using Celref program. The calculated lattice parameters and unit cell volume are given in Table 1.

Table 1. Structural parameters calculated from XRD data of the studied samples

Lattice parameters and unit cell volume	x (%)				
	30	**33**	**36**	**39**	**42**
Structure	T	T	T	T	T
a=b (Å)	3.9998	3.9932	3.9964	3.9944	3.9941
c (Å)	4 .0552	4.0634	4.0522	4.0554	4.0556
c/a	1.0138	1.0175	1.0144	1.0152	1.0153
V(Å³)	64.87	64.79	64.71	64.70	64.69

Notes: **T:** means tetragonal structure.

It can be seen from tetragonal distortion ratio (c/a) values that the addition of Cr, Ni, and Sb to PZT does not affect significantly the tetragonality of lattice structure.

3.2 Sintering temperature

Ceramic material properties strongly depend to its physical density; ceramics having high density are expected to have better properties. Sintering is a thermal process used to remove void spaces between the ceramic powder particles, causing densification and shrinkage of the component which lead to give perfect microstructure without any cracks or defects. The optimal sintering temperature can be determined from density variations as a function of sintering temperature; the optimal sintering temperature is the temperature where sample density is maximal. Table 2 presents the density values of the PZT-CNS ceramics at different sintering temperatures. It can be observed that the maximum density was found at a sintering temperature T = 1180 °C.

Table 2. PZT-CNS density variations as a function of sintering temperature

Samples	$D_{1100\ °C}$	$D_{1150\ °C}$	$D_{1180\ °C}$	$D_{1200\ °C}$
F1	7.2925	7.3084	7.3320	7.3133
F2	7.1220	7.2538	7.3004	7.2667
F3	7.2917	7.3288	7.3505	7.3452
F4	7.2780	7.3010	7.3981	7.3748
F5	7.2817	7.3459	7.4355	7.3713

Notes:
F1: 0,20$PbZrO_3$-0,30$PbTiO_3$-0,50Pb ($Cr_{1/5}Ni_{1/5}Sb_{3/5}$) O_3
F2: 0,20$PbZrO_3$-0,33$PbTiO_3$-0,47Pb ($Cr_{1/5}Ni_{1/5}Sb_{3/5}$) O_3
F3: 0,20$PbZrO_3$-0,36$PbTiO_3$-0,44Pb ($Cr_{1/5}Ni_{1/5}Sb_{3/5}$) O_3
F4: 0,20$PbZrO_3$-0,39$PbTiO_3$-0,41Pb ($Cr_{1/5}Ni_{1/5}Sb_{3/5}$) O_3
F5: 0,20$PbZrO_3$-0,42$PbTiO_3$-0,38Pb ($Cr_{1/5}Ni_{1/5}Sb_{3/5}$) O_3

3.3 Density and porosity of PZT-CNS ceramics

Density and porosity variations for PZT-CNS ceramics as a function of x proportion are shown in figure 3. It can be observed that the density decreases for x = 33 %. Then, this physical parameter increases until reaching a maximum value (92.93 % of theoretical density) at x = 42 %. Conversely, the porosity was found to increase at x=33 %, and then decreases to get minimum value at x=42 %. These reported variations are in good agreement with the microstructure observed for the different samples.

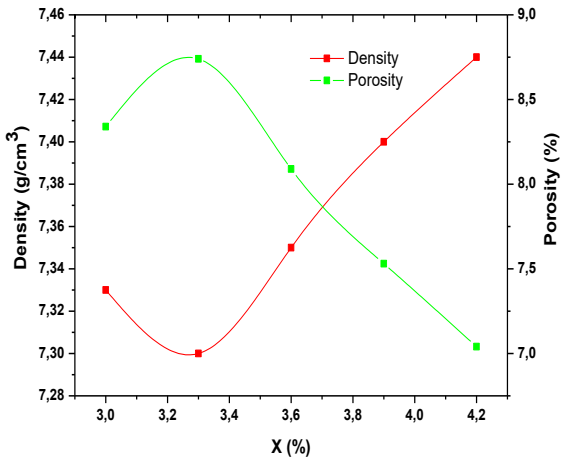

Figure 3. Density and porosity variations for PZT-CNS ceramics

3.4 Microstructure of the studied ceramics

The microstructure quality of a ceramic material can strongly affect the resulting properties such as dielectric constant, electronic conductivity, and heat transfer. High compact microstructure is required for maximum properties enhancement. Scanning electron microscopy SEM can be used to study the microstructure characteristics of ceramic materials. SEM micrographs presented in Figure 4 show the microstructure of PZT-CNS ceramics under probe.

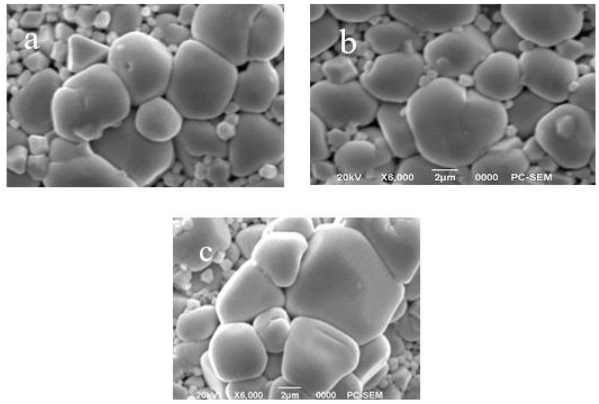

Figure 4. SEM images of (0.80-x)Pb($Cr_{1/5}$,$Ni_{1/5}$,$Sb_{3/5}$)O_3-x$PbTiO_3$-0.20$PbZrO_3$ ceramics sintered at 1180 °C for 2 h, (a) Ti = 36; (b) Ti = 39; (c) Ti = 42

It is apparent that the studied samples have a microstructure composed by grains of different shapes and sizes. The grain boundaries are compact and small number of pores is appeared. The average grain size values corresponding to the PZT-CNS samples are collected in Table 3. We observe that the average grain size increases from 1.842 µm for the sample containing 36 % to 2.521 µm for the sample containing 42 % of Ti, which confirms that titanium has a positive effect on the density of samples.

Table 3. Average grain size of the studied samples

Sample	Average grain size (µm)
PZT-CNS (Ti=36%)	1.842
PZT-CNS (Ti=39%)	2.283
PZT-CNS (Ti=42%)	2.521

3.5 Dielectric properties of PZT-CNS ceramics

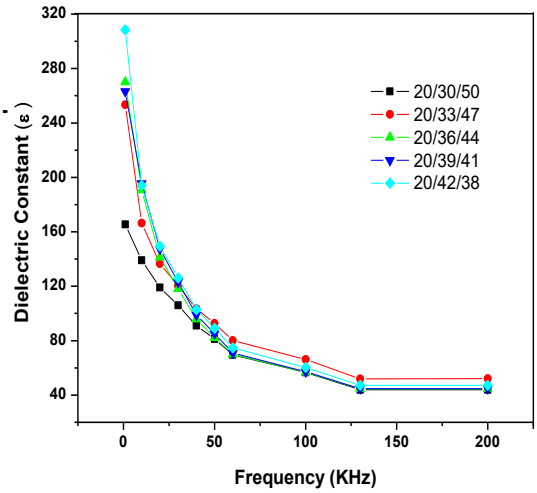

Figure 5. Evolution of the dielectric constant as function of frequency

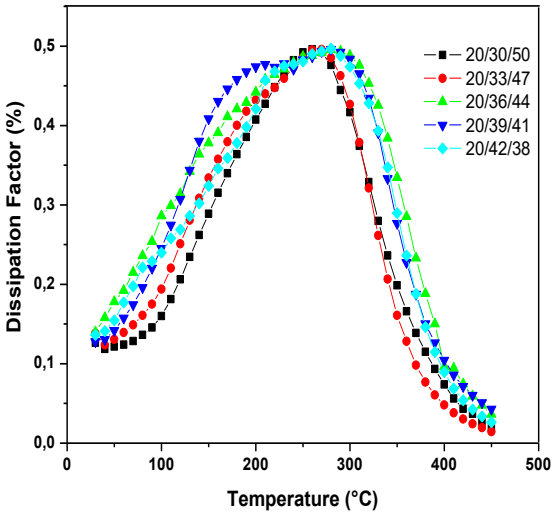

Figure 6. Temperature dependence of dissipation factor for PZT-CNS ceramics

The dielectric behavior of ceramic materials under an external electric field has gained great interest of numerous papers, in view of its high scientific and technological importance. Dielectric measurement is an important experimental test, which can be used to enrich knowledge of ceramic materials with respect to other electrical properties. Based on the experimental data of these measurements, dielectric parameters including dielectric constant ε′ and dissipation factor (tanδ) can be calculated as mentioned in the experimental part (Eq. (3) and Eq. (4)). In the present investigation, the frequency and temperature dependences of dielectric parameters for PZT-CNS ceramics were analyzed.

Experimental results displayed in Figure 5 show the variations of dielectric constant of the studied ceramics sintered at 1180 °C as a function of frequency.

It can be seen that the dielectric constant decreases with increasing of frequency. The decrease in dielectric constant may be attributed to the polarization decreasing with increasing frequency [17]. Additionally, the dielectric constant increases with the increasing of Ti amount.

Dissipation factor is a measure of loss-rate of the electrical energy, usually in the form of heat propagation. When a material is to be used in electric applications where high capacitance is needed, a lower dissipation factor is required. The variations of the dissipation factor with temperature for the PZT-CNS ceramics sintered at 1180 °C were measured in the temperature range 25-450 °C and shown in Figure 6. It can be seen that all PZT-CNS samples exhibit a dissipation factor < 0.6 %.

4. CONCLUSION

PZT containing Cr, Ni, and Sb dopants named PZT-CNS ceramics have been successfully prepared by a solid-state reaction method. The effects of sintering temperature and titanium content on structural, morphological, and electrical properties have been investigated. XRD results declared that PZT-CNS ceramics have a pure tetragonal perovskite phase. Density and porosity results revealed that the optimum sintering temperature was found to be 1180 °C. The reported experimental findings showed that Ti amount between 30 and 42 % has a positive effect on the properties of the elaborated PZT-CNS properties. $0.20PbZrO_3$-$0.42PbTiO_3$-$0.38Pb(Cr_{1/5},Ni_{1/5},Sb_{3/5})O_3$ sample exhibited the best properties.

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