IN MEMORIAM Prof. Dr. Ing. PETRU BALTĂ

PROPRIETĂȚILE STRUCTURALE ŞI DIELECTRICE ALE COMPOZIȚIILOR CERAMICE DE $Sr_{0,5}Ba_{0,5}Nb_2O_6$ DOPATE CU CALCIU
STRUCTURE AND DIELECTRIC PROPERTIES OF Ca DOPED $Sr_{0.5}Ba_{0.5}Nb_2O_6$ CERAMIC COMPOSITIONS

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Calcium doped strontium barium niobate $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN:50) is a tungsten bronze ferroelectric material with a tetragonal unit cell. $Sr_xCa_yBa_{1-x-y}Nb_2O_6$ (SCBN) compositions with (x = 0.5; y = 0.14 and 0.28) were obtained by solid-state reaction method. The phase structure, microstructure and dielectric properties of obtained SCBN ceramics were systematically investigated. XRD results showed that SCBN phase with tungsten bronze structure could be obtained in all ceramic samples. Higher Ca content (y = 0.28) lead to occurrence of a secondary phase of $CaNb_2O_6$. SEM micrographs show the formation of crystallites with sharp boundaries with an average grain size of about 4 ÷ 12 µm for all SCBN compositions. Compared with pure SBN:50 composition, Ca doping results in a reduction of the dielectric constant value, but the dielectric losses are found to be smaller for this compositions.

Niobatul de stronțiu şi bariu dopat cu calciu $Sr_{0,5}Ba_{0,5}Nb_2O_6$ (SBN:50) este un material feroelectric cu structură tetragonală de tip tungsten bronze. Compozițiile de $Sr_xCa_yBa_{1-x-y}Nb_2O_6$ (SCBN) cu (x = 0,5; y = 0,14 şi 0,28) au fost obținute prin reacție în fază solidă. Structura, microstructura şi proprietățile dielectrice ale ceramicilor obținute au fost sistematic investigate. Analizele de difracție a razelor X au indicat pentru toate probele ceramice de SCBN obținerea fazei tetragonale de tip tungsten bronze. Creşterea conținutului de calciu (y = 0,28) duce la apariția unei faze secundare de $CaNb_2O_6$. Micrografiile SEM indică pentru toate compozițiile de SCBN limite granulare bine definite şi dimensiuni ale granulelor cuprinse între 4 ÷ 12 µm. În comparație cu compoziția etalon SBN:50, dopajul cu calciu are ca efect scăderea valorii constantei dielectrice însă, pierderile dielectrice sunt mai mici în cazul acestor compoziții.

Keywords: *SBN, SCBN, TTB structure, Dielectric properties*

1. Introduction

Pure and doped strontium barium niobate ceramics have been studied extensively for their important pyroelectric, piezoelectric, electro-optic and photorefractive applications. $Sr_xBa_{1-x}Nb_2O_6$ (SBN) system with $0.25 \leq x \leq 0.75$ is a ferroelectric solid solution between $SrNb_2O_6$ and $BaNb_2O_6$ which exist in a tetragonal tungsten bronze (TTB) structure [1,2]. The TTB compositions are characterized by the chemical formula $[(A1)_2(A2)_4C_4][(B1)_2(B2)_8]O_{30}$, in which the A1, A2, B and C sites are 15-, 12-, 6- and 9- fold coordinated oxygen octahedral sites in the crystal lattice structure. The A1 and A2 sites can be occupied by Sr^{2+}, Ba^{2+}, Ca^{2+}, Pb^{2+}, K^+, Na^+ and some rare earth cations, B sites by Nb^{5+} or Ta^{5+} and the C sites by Li^+ and other small cations. The smallest C sites are usually empty, and then the formula $A_6B_{10}O_{30}$ is for the filled tungsten bronze structure [3-5].

The properties of SBN are very sensitive to the amount and type of substitution, method of preparation and sintering conditions [6]. SBN compositions has been reported to have been synthesized with different Sr:Ba ratio using various methods, such as solid-state reaction synthesis, sol-gel route, solution combustion, coprecipitation and partial coprecipitation [2,7-9].

Despite the high exhibited values of electro-optic and pyroelectric coefficients, SBN compositions have a relatively low Curie temperature (50 ÷ 150°C) and high dielectric losses ($tg\ \delta$ = 0.03 ÷ 0.14) which limits the use of these materials in practical applications. The reported values for the dielectric constant of SBN compositions measured at room temperature and at various frequencies are between (ε_r = 500 ÷ 1500) [2,8,10-12].

Adding calcium into SBN structure will determine the formation of a mixed crystal $Sr_xCa_yBa_{1-x-y}Nb_2O_6$ which could present superior

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dielectric behavior due to the smaller radius of calcium ions.

The Ca doped $Sr_xBa_{1-x}Nb_2O_6$ (x = 0.5, SBN:50) ceramic samples were obtained by solid-state reaction method and systematically investigated in comparison with undoped SBN:50 composition. Synthesis procedure and dielectric properties for pure SBN:50 ceramic sample was discussed in a previous article [13].

2. Experimental

M. Muehlberg et al. designed for $Sr_xCa_yBa_{1-x-y}Nb_2O_6$ ($0 < x,y < 1$, SCBN) mixed crystals the phase diagram of the quasi-ternary system $CaNb_2O_6$ - $SrNb_2O_6$ - $BaNb_2O_6$ with a limited area in which single TTB phase of SCBN occurs. For (x = 0.5) the domain of SCBN single phase existence is between $0 \le y_{Ca} \le 0.35$ [14]. In present paper are used two values for Ca doping SBN:50 (0.14 and 0.28) to point out the influence of calcium doping over dielectric behavior.

Polycrystalline $Sr_{0.5}Ca_{0.14}Ba_{0.36}Nb_2O_6$ (SCBN:50/14) and $Sr_{0.5}Ca_{0.28}Ba_{0.22}Nb_2O_6$ (SCBN:50/28) ceramic compositions were obtained by solid-state reaction method. The starting raw materials were reagent grade $SrCO_3$, $BaCO_3$, $CaCO_3$ and Nb_2O_5 as received. A flow diagram of the experimental procedure is given in Figure 1.

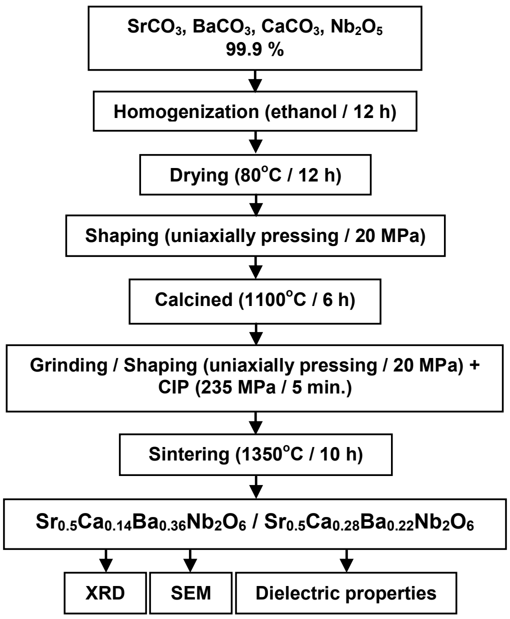


Fig. 1- Flowchart of SCBN ceramics preparation / *Fluxul tehnologic de preparare al ceramicilor de SCBN.*

The micropowders of $SrCO_3$, $BaCO_3$, $CaCO_3$ and Nb_2O_5 were mixed in stoichiometric proportions and homogenized in ethanol medium for 12 h. The slurry was dried at 80°C, uniaxially pressed (at 20 MPa) into pellets and calcined at 1100°C for 6 h in air, in order to obtain a single phase. Then, the calcinated samples were grinded in the agate mortar, the powders were compacted uniaxially (at 20 MPa) into discs with 10 mm diameters and cold isostatic pressed (CIP) at a pressure of 235 MPa for 5 min. All samples were then sintered in air at 1350°C for 10 h to obtain dense ceramic pellets.

Densities of the sintered samples were determined based on the Archimedes method using xylene as the displacement fluid. The relative density was around 97.83% for SCBN:50/14 ceramic sample and 98.12% for SCBN:50/28 composition.

The structure of the SCBN:50/14 and SCBN:50/28 ceramic samples were analyzed by X-ray diffraction XRD (PANalytical X'Pert PRO MRD, Netherlands). Microstructure was observed using a scanning electron microscopy SEM (Quanta Inspect F, Netherlands) with EDAX option. Dielectric properties were analyzed by an impedance analyzer (HP / AGILENT 4194A equipped with 16451B dielectric test fixture) with a frequency swept in steps from 1 kHz to 5 MHz.

3. Results and discussion

3.1. Phase composition and structural parameters

Figure 2 shows the XRD patterns of the SCBN:50/14 and SCBN:50/28 compositions sintered at 1350°C for 10 h.

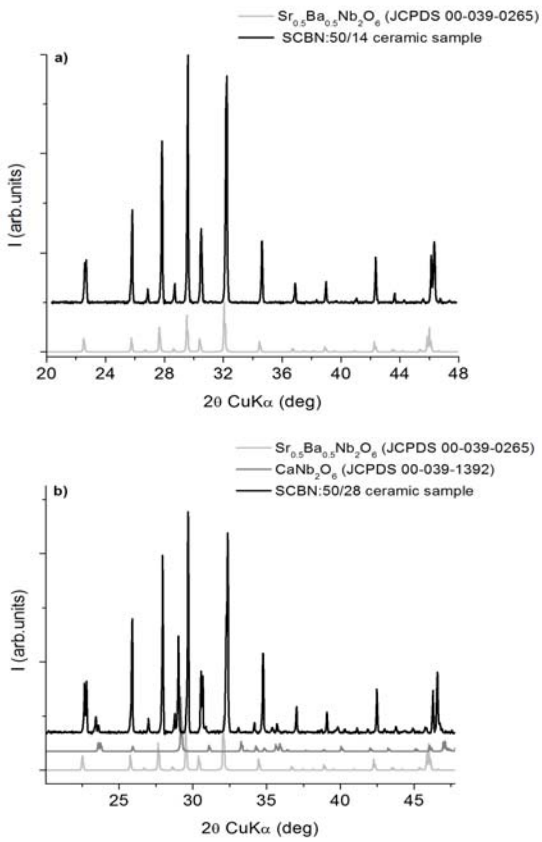


Fig. 2 - XRD patterns of SCBN ceramics: a) SCBN:50/14; b) SCBN:50/28 / *Difractogramele XRD ale ceramicilor de SCBN: a) SCBN:50/14; b) SCBN:50/28.*

For SCBN:50/14 ceramic sample, all the diffraction peaks indicates that the sample are crystallized into a pure TTB structure without secondary phases, in good agreement with their corresponding pdf card for $Sr_{0.5}Ba_{0.5}Nb_2O_6$ composition (JCPDS 00-039-0265). Instead, the SCBN:50/28 ceramic sample XRD pattern exhibits a mixture of a TTB as major phase with an orthorhombic phase of $CaNb_2O_6$ (JCPDS 00-039-1392).

It was observed the presence of a secondary phase ($CaNb_2O_6$) in sample with a higher proportion of Ca^{2+} (0.28). This could means that a higher proportion of calcium could not be integrated in SBN:50 structure and that the secondary phase is obtained directly from the raw materials.

The calculated unit cell parameters are presented in Table 1 in comparison with their corresponding JCPDS file.

Table 1

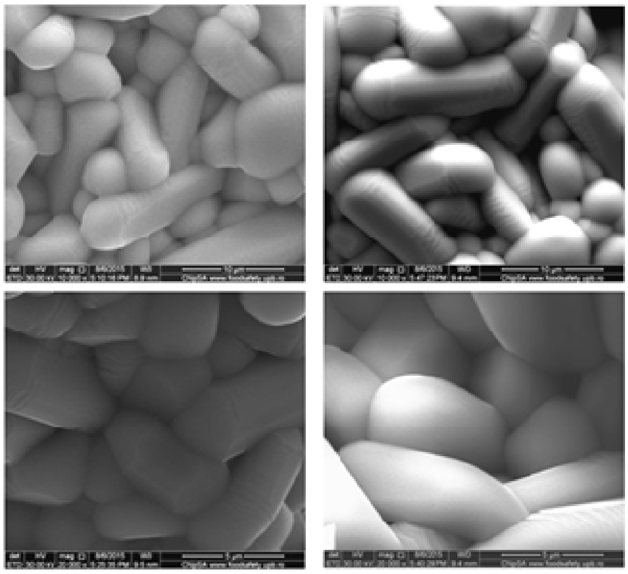
Structural data / *Date structurale*

Sample	Cell parameters		
	a (Å)	**c (Å)**	**V (Å^3)**
$Sr_{0.5}Ba_{0.5}Nb_2O_6$ (JCPDS 00-039-0265)	12.465	3.952	614.08
SBN:50 [13]	12.485	3.948	615.13
SCBN:50/14	12.421	3.904	602.57
SCBN:50/28	12.392	3.901	598.60

SCBN:50/14 ceramic sample is crystallized into a pure TTB phase but the cell parameters are significantly smaller than pure SBN:50 composition [13]. This can be explained by the smaller ionic radius of calcium which is integrated in SBN:50 structure. With increasing of calcium content (SCBN:50/28 sample) a TTB structure with a smaller volume is still obtained but along with a secondary phase, an orthorhombic $CaNb_2O_6$.

3.2. Microstructure

Figure 3 shows the SEM morphology of fractured surfaces of SCBN compositions. The samples exhibit a good densification and well grown columnar grains with triple junction at angle between the grain boundaries of ~ 120^o. The average grain size were ~ 4 μm in diameter and 10 ÷ 12 μm in length. From SCBN:50/28 ceramic sample, grains of the second phase $CaNb_2O_6$ could not be identified from the grains of the SCBN phase.



a) b)

Fig. 3 - SEM images of fractured surface of SCBN ceramics: a) SCBN:50/14; b) SCBN:50/28 / *Imagini SEM ale ceramicilor de SCBN realizate în secțiune: a) SCBN:50/14; b) SCBN:50/28.*

For all samples the EDAX results confirmed the existence of the elements corresponding to the SCBN compositions (Fig. 4).

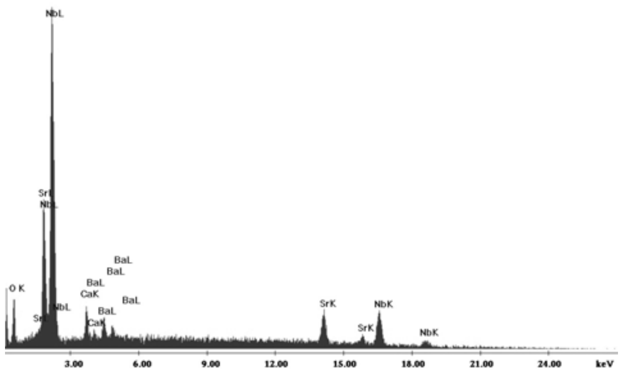


Fig. 4. - EDAX spectrum for SCBN:50/28 ceramic sample / *Spectru EDAX pentru proba ceramică SCBN:50/28.*

3.3. Dielectric properties

Dielectric properties evidenced by dielectric constant (ε_r) and dielectric loss ($tg\ \delta$) values recorded at 1 MHz around room temperature are presented in Figure 5. The dielectric constant value was calculated using plan capacitance approximation.

For SCBN:50/14 sample the value were found to be ε_r ~ 270 and ε_r ~ 160 for SCBN:50/28 sample, respectively. The dielectric losses are smaller for SCBN:50/28 composition (*tg δ* ~ 0.041) than the SCBN:50/14 composition (*tg δ* ~ 0.057).

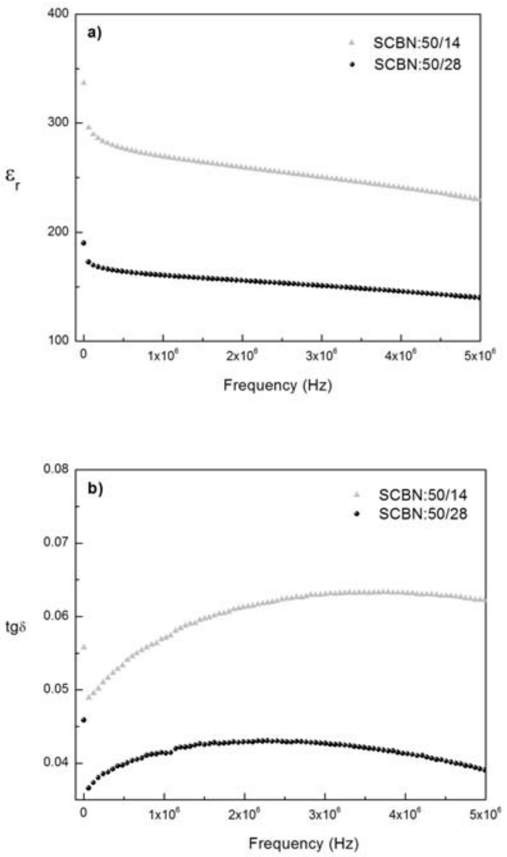


Fig. 5 - Dielectric properties (ε_r and *tg δ*) for SCBN ceramic samples / *Valorile proprietăților dielectrice (ε_r şi tg δ) pentru probele ceramice de SCBN.*

Compared with the dielectric properties of pure SBN:50 ceramic sample (ε_r ~ 488 and *tg δ* ~ 0.097) measured at 1 MHz [13] and other literature data [2,10-12], the SCBN compositions show smaller values for the dielectric constant. It is obviously that the dielectric constant value was reduced with increased of Ca content. The decrease became more serious with the formation of $CaNb_2O_6$ phase as shown in SCBN:50/28 ceramic sample. Instead, the dielectric losses are lower for these compositions, an important issue for this type of materials.

4. Conclusion

Tungsten bronze structure of $Sr_xCa_yBa_{1-x-y}Nb_2O_6$ ceramics (*x* = 0.5; *y* = 0.14 and 0.28) were prepared by the conventional solid-state reaction method.

The phase structure, morphology and dielectric properties of prepared ceramics as a function of Ca content were investigated. The XRD results showed that pure tungsten bronze structure was obtained in all ceramic samples. Higher Ca content (*y* = 0.28) lead to occurrence of a secondary phase in $Sr_{0.5}Ca_{0.28}Ba_{0.22}Nb_2O_6$ composition. SEM results show a good densification and clear crystalline boundaries for all SCBN samples.

For SCBN:50/14 composition the dielectric constant value is higher than SCBN:50/28 ceramic sample but, the dielectric losses are lower for this composition. Finally, $Sr_xCa_yBa_{1-x-y}Nb_2O_6$ (*x* = 0.5; *y* = 0.14 and 0.28) compositions are suitable to be used as ceramic target for obtain thin layers by physical deposition methods.

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