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Structural Effects and their Correlation with Dielectric Responsive and Dissipative Properties of BSN Ceramics

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Abstract

The paper discusses the study of the structure of dielectric and dissipative characteristics of ceramics of solid solutions of the system $Ba_{1-x}Sr_xNb_2O_6$ ($0.0 \leq x \leq 1.0$, $\Delta x = 0.1$). On the basis of the results the phase diagram was plotted, and it was established that macroproperties of solid solutions have anomalies adjacent to boundaries, and the change of types of solid solutions accompanied by the increase of Sr content leads to the growth of relaxation properties. Also, prospects of certain compounds for application as radiowave-absorbing materials was demonstrated.

Keywords: Solid Solutions, Niobates of Alkaline-Earth Metals, Phase Diagram, Relaxation Properties, Radiowave-Absorbing Materials

Introduction

Interest for solid solutions (SS) based on niobates of alkaline-earth metals, which are numerous class of ferroelectric materials with structure consisting of tetragonal tungsten bronze (TTB), in particular $Ba_{1-x}Sr_xNb_2O_6$ (BSN), is related to their specific properties and, therefore, prospects for application in pyroelectric receivers and transformers of image, optical storage devices, modulators, deflectors, laser equipment [1], as well as with practically exhausted engineering potential of known perovskite medias. However, in spite of attractiveness of that kind of materials from the point of view of material science, their wide application is limited by technological complications, election of certain research chemical compounds, as well as by the absence of information on the relationships of macroscopic properties (dielectric, piezoelectric, etc.) and the features of their crystalline structure. Boundary components of the discussed system are $BaNb_2O_6$ and $SrNb_2O_6$. The first has two polymorphous modifications [1], one of which has hexagonal symmetry and is stable in a narrow temperature range lower (but close) to melting temperature, another (low-temperature) phase has rhombic symmetry (R) with a = 12.17 Å, b = 10.25 Å, c = 3.94 Å. The study [2] reports that this phase is ferroelectric (FE), but the study [3] doesn't confirm that. $SrNb_2O_6$ is not FE, which has complex structure, but is not isomorphous to $BaNb_2O_6$ [4]. The base of the structure of BSN is 3D structure, which is formed by NbO_6 octahedron and which forms three types of structural channels: the narrowest, with triangular cross-section (C, trigonal) are not filled; with medium transversal dimensions and rectangular shape (A1, tetragonal), which are settled with Sr atoms; and the ones with the largest volume and of pentagonal shape (A2, pentagonal) are simultaneously settled with Ba and Sr atoms, or by only one of them, depending on concentration of boundary components of the system [1]. In the study [5] structure of SS BSN in the range of 93-423 K was identified by electron diffraction method and it was established that it randomly oriented serial microdomain texture of one-dimensional incommensurate superstructures, which include two components with orthorhombic symmetry. In the study [6] it is stated that BSN crystals belong to structure of non-filled tungsten bronze, in which statistically

settled are only 5/6 of cation positions, which leads to disorder in crystal chemistry condition [7]. Detailed studies of BSN ($0.4 \le x \le 0.6$) by means of the method of Raman spectroscopy were carried out in the work [8], and they verified structure of tungsten bronze in those tetragonal (T) (4/mmm-C4v) SS. It was noted that for all FE with that structure there is disorderly oriented polarization at temperatures, which are much higher than Curie temperature (T_C), which allows to classify those SS as FE with glassy phase. In the studies [9-10] two FE phases were identified in the system: T-at $0.4 \le x \le 0.45$ and R-at $0.6 \le x \le 0.8$. In the study [11] on the basis of the analysis of correlation composition-structure-properties of several compositions of BSN the authors demonstrated that the decrease of Sr/Ba decreases settlement of only A2 structural channels, increases splitting of positions of Ba and Sr atoms (i.e., their nonequivalence) in channels and values of shifts of Nb ions from centers of octahedrons. The authors of the presented paper in the works [12-15] demonstrated that it is possible by means of optimization of production condition of SS BSN to obtain pure ceramics and thin films having strength and high density, which are based on large-scale BSN-targets.

Objects, Methods of Production and Study of Specimens

The objects of study were SS $Ba_{0.5}Sr_{0.5}Nb_2O_6$. In the presented paper we discuss continuous series of SS of $Ba_{1-x}Sr_xNb_2O_6$ type ($0.0 \le x \le 1.0$).

Synthesis of the specimens was carried out using the method of solid-state reactions by firing in two stages at the following temperatures and exposure times: T_1 = 1350-1375 °C, τ_1 = 10 h, T_2 = 1375-1400 °C, τ_2 = 2 h, depending on composition with grinding between the stages; sintering of ceramic workpieces at T = 1375-1400 °C during τ = 2 h. Radiographic studies included powder X-Ray diffraction using DRON-3 diffractometer (Bragg-Brentano focusing scheme) with Co_{K_α}-radiation. Parameters of SS cell from T zone of phase diagram were calculated taking into account that TTB is incommensurate structure, in which positions of oxygen atom and effective atom Sr/Ba are modulated in pentagonal channels. Therefore, c parameter of T-cell is doubled, and the number of formula units at one cell is increasing in 10 times. Only at that condition relative density of the studied ceramics, which is calculated as ratio of density measured by weighting in octane and X-ray measured density, has the real value of 90-93%, which is almost the limiting value for SS, which are produced using the described method (if the calculation is carried out according to [7], relative densities will considerably exceed 100% (114-118%)).

Temperature relationship of relative dielectric permeability ($\varepsilon/\varepsilon_0$) in temperature ranges T = 25-500 ºC and frequencies f = 25-10^6 Hz were studied at the laboratory bench "YuKOMP 2.0". For experimental studies of dissipative properties of materials in frequency range of 1-9 GHz we used the device based on network analyzer E8363B [16]. As the main parameter characterizing microwave absorption of electromagnetic radiation we used element of scattering matrix S_{21}.

Experimental Results and Discussion

Fig. 1a presents X-Ray diffraction patterns of $BaNb_2O_6$, $SrNb_20_6$ and SS from various zones of the phase diagram. For the selected parameters of production $BaNb_2O_6$ crystallizes with R symmetry with the following cell parameters: a = 12.180 Å, b = 10.268 Å, c = 7.855 Å, V = 982 Å^3; that results are in good agreement with the data from the study [17], in which it is established that for sintering at temperatures higher than 1310 ºC R phase of $BaNb_2O_6$ is stable. Metaniobate of strontium has monoclinic (M) symmetry with a = 7.719 Å, b = 5.589 Å, c = 10.984 Å, β = 90.35º, which is also almost coincide with the results in the study [17].

Fig. 1b shows relationship of cell parameters and x, dotted lines represents stability boundaries of phases. Phase diagram has the following form: in the range $0.0 \le x < 0.2$ there are SS with R structure $BaNb_2O_6$-R-phase; at $0.0 < x \le 0.1$ there are R-phase and SS with TTB structure, which we specified as T-phase, formed in the range $0.1 \le x \le 0.8$; at $0.7 < x \le 0.8$ there are T-phase and SS with monoclinic $SrNb_20_6$ type structure-M phase; in the range $0.8 < x \le 1.0$ there is M-phase. It can be seen that near $BaNb_2O_6$ and $SrNb_2O_6$ parameters and volume of cell doesn't change. In the range $0.0 < x \le 0.1$ parameters a, b and V of R-cell are increasing, in spite of substitution of Ba^{+2} (R = 1.38 Å) with smaller Sr^{+2} (R = 1.20 Å). It means that the latter is embedding into A1 positions in rectangular channels, where there is no Ba. T-phase is divided into 2 main concentration regions: at $0.1 \le x \le 0.4$ structural parameters change nonmonotonously, and at $0.4 \le x \le 0.7$ parameters monotonously decrease. In the first zone according to the relationship V(x), at x = 0.1-0.2 the main factor is settlement of A1 positions, at x = 0.2-0.3-substitution of $Sr^{+2} \rightarrow Ba^{+2}$ in positions of A2 in pentagonal channels, at x = 0.3-0.4-again settlement of positions of A1.

In the second regions, where cells are monotonously decreasing, it is obvious, that only substitution of $Sr^{+2} \rightarrow Ba^{+2}$ takes places in positions of A2 in pentagonal channels, which conforms with the results of studies of monocrystals in the study [18]. In that study we investigated into properties of crystals in the range $0.32 \le x \le 0.82$, and it was demonstrated that in the range $x \approx 0.35$-0.45 positions of A1 are settled with Sr, correspondingly, from 66% to 72% and simultaneously substitution of $Sr^{+2} \rightarrow Ba^{+2}$ in positions of A2 takes place. At $x > 0.45$ amount of Sr in tetragonal channels doesn't change, and only substitution of ions in pentagonal channels occurs. It is worth mentioning that according to the data from the study [18] in congruously melting SS amount of Sr and Ba in pentagonal channels is almost the same. Thus, in BSN ceramics as well as in monocrystals [18], increase of Sr concentration formation of TTB structure has two stages: in the range x = 0.1-0.4 positions of A1 and A2 (SS1) are settled, but in that range one of the two processes takes dominating places in alternating manner. At $x > 0.4$ settlement of positions of A1 ceases and only substitution if $Sr^{+2} \rightarrow Ba^{+2}$ in positions of A2 (SS2) takes place. Thus, near $x \sim 0.45$ there is the configuration shift between two isomorphic SS (SS1→SS2).

Fig. 2 shows the relationships of $\varepsilon/\varepsilon_0(T)$ ceramics with x = 0.2-0.7 (Δx = 0.1) in the discussed range of temperature and frequencies, which were obtained in the cooling mode; Fig. 3 demonstrates concentration relationship of Curie temperature, T_C, corresponding to maximum at the curve $\varepsilon/\varepsilon_0(T)$ with frequency of 10^6 Hz, $\varepsilon/\varepsilon_0$ at T = 30°C ($(\varepsilon/\varepsilon_0)_{30°C}$) and at $T = T_C$ ($(\varepsilon/\varepsilon_0)_{max}$), $(\Delta\varepsilon/\varepsilon_0)_{30°C} = \varepsilon/\varepsilon_0(T = 30°C, f = 200$ Hz)-

$\varepsilon/\varepsilon_0$($T$ = 30°C, f = 10^6 Hz) and S_{21max}. It is obvious that there is correlation between dielectric responses and values of S_{21} and phase portrait of the system: macroproperties of SS show anomalies near phase boundaries and during changes of modes of SS, at that, increase of Sr content leads to increase of relaxation properties, which is accompanied by large-scale diffusion and shift in the direction of room temperatures of the zone of ferroelectric-paraelectric phase shift, which conforms with the data from [11].

It is worth mentioning that alongside with the known applications of BSN ceramics, compositions with high S_{21} (x ~ 0.6) can be implemented as radiowave-absorbing materials.

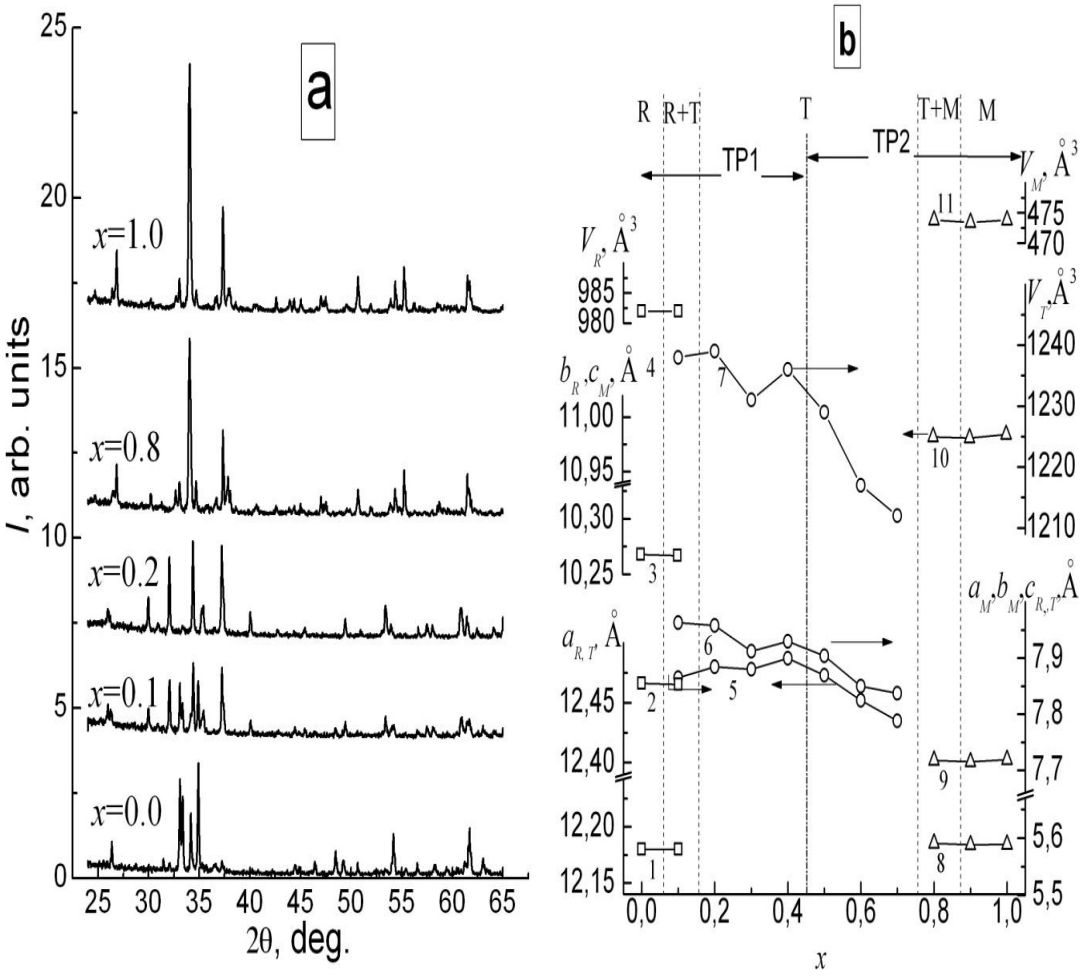

Figure 1a: X-Ray diffraction patterns of ceramics $BaNb_2O_6$, $Sr_{0.1}Ba_{0.9}Nb_2O_6$, $Sr_{0.2}Ba_{0.8}Nb_2O_6$, $Sr_{0.8}Ba_{0.2}Nb_2O_6$ и $SrNb_2O_6$ at room temperature.

b: relationships of parameters and volume of cells of SS $Ba_{1-x}Sr_xNb_2O_6$ and x: 1-a_R, 2-c_R, 3-b_R, 4-V_R-rhombic, 5-a_T, 6-c_T, 7-V_T-tetragonal, 8-a_M, 9-b_M, 10-c_M, 11-V_M-monoclinic.

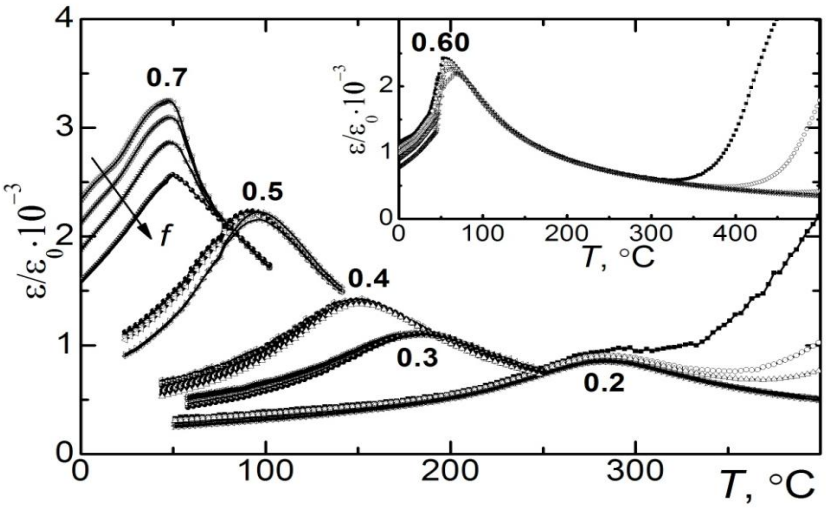

Figure 2: Relationships of $\varepsilon/\varepsilon_0(T)$ ceramics of SS with x=0.2-0.7 (Δx=0.1) in ranges of temperatures T = 25-400 °C and frequencies f = 200-10^6 Hz, obtained in cooling mode. The arrow shows the direction of the increase of f. Numbers near the curve correspond to the values of x.

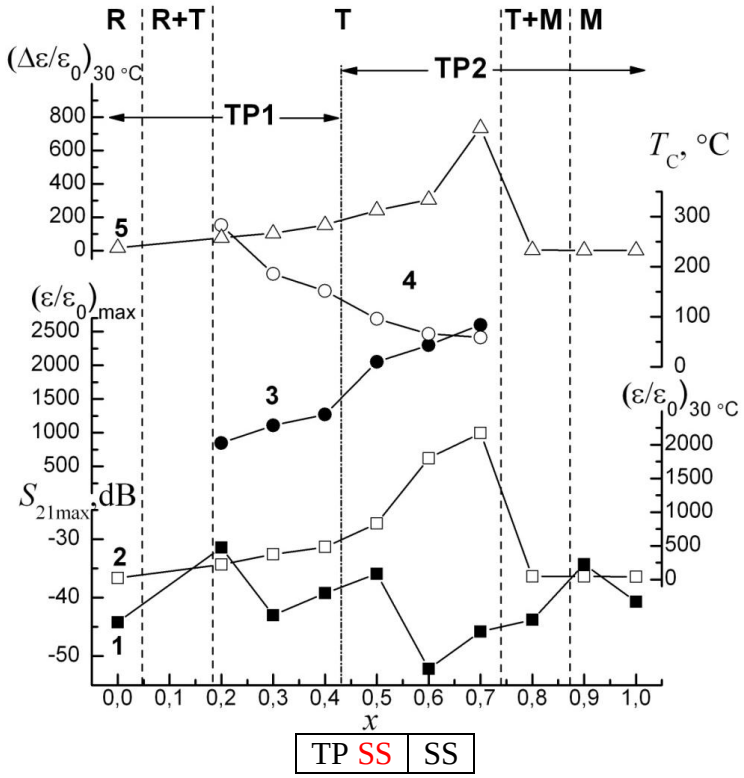

Figure 3: Concentration relationships of S_{21max}-1, $(\varepsilon/\varepsilon_0)_{30°C}$-2, $(\varepsilon/\varepsilon_0)_{max}$-3, T_C-4 and $(\Delta\varepsilon/\varepsilon_0)_{30°C}$-5.

Conclusion

The study presents the investigation of the structure of dielectric and dissipative characteristics of ceramics of solid solutions of the system $Ba_{1-x}Sr_xNb_2O_6$ ($0.0 \leq x \leq 1.0$, $\Delta x = 0.1$).

It was established that in case of the increase of Sr concentration the formation of the structure of TTB SS has two stages: in the range $x = 0.1$-0.4 positions of A1 and A2 (SS1) are settled, at $x > 0.4$ settlement of positions of A1 ceases and only substitution of $Sr^{+2} \rightarrow Ba^{+2}$ in positions of A2 (SS2) takes place, in other words, near $x \sim 0.45$ there is configuration shift between two types of isomorphic SS.

The results show correlation between dielectric responses and values of S_{21} and phase portrait of the system: macroproperties of SS show anomalies near phase boundaries and during change of SS types.

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