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Influence of vanadium dopant on relaxor behavior of $BaBi_2Nb_2O_9$ ceramics

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Abstract

The article reports the successful preparation of single-phase vanadium doped $BaBi_2Nb_2O_9$ ceramics. In the first part of the paper we would like to present the results of the XRD measurements, which allows us to determine the lattice parameters. The parameters do not change, which implies that the vanadium ions ordering of the crystal structure causes the decreasing number of defects. The conclusion stays consistent with the results of dielectric and thermal stimulated depolarization currents measurements, described in the second part of the paper. The pure BBN ceramics, as well as the ones modified by vanadium, show the frequency dependence of the dielectric response typical for relaxor ferroelectrics i.e. the significant reduction of *SYMBOL 101 \f ''Symbol'' \s 12e'$_{max}$* and shift of the corresponding temperature (T_m) towards higher values with the frequency increase. However the vanadium substitution causes a reduction of the value of parameters describing the relaxor properties.

Keywords: Aurivillius; Relaxor; TSD; SEM

1. Introduction

The lead free materials that belong to Aurivillius, especially $SrBi_2Ta_2O_9$ (SNT) and $SrBi_2Nb_2O_9$ (SBN), are very interesting due to their excellent polarization fatigue-free behavior and low leakage currents [1,2]. However modern industrial applications also require high mechanical quality. This aspect is closely related to the microstructure of the ceramics. Namely the ceramics with the well-developed grain structure, which means that the shape of grains is close to regular polygons, characterized by high degree of compaction and small pore number. These features determine the high density of ceramics and good mechanical properties. Based on literature [3,4] a very promising improvement to these features seems to be vanadium dopant. In case of SBN ceramics this dopant remarkably improved not only the quality of ceramics, but also the dielectric properties. Moreover the admixture of vanadium is responsible for change in the grain shape from oval to a lamella plate pattern. This fact indicates a creation of a liquid phase during the sintering process connected with low melting point of vanadium oxide (~699 °C), which increased significantly the mechanical quality of this ceramics [5]. Moreover, substituting niobium atom by vanadium with a lower ion radius (69 pm–58 pm, respectively) should result in lattice parameters reduction. An investigation of this issue revealed such behavior does not happen until 15 at%, caused probably by $(Bi_2O_2)^{2+}$ layers which prevented perovskite unit cell shrinkage [6]. Because the influence of these layers is limited, therefore after crossing the same tension limit of the structure the shrinking process is however activated. The discussed difference in vanadium and niobium ion radiuses and lack of structure shrinkage phenomena lead to the decrease of the packing degree of ions in the distorted oxygen octahedral $Nb(V)O_6$ of perovskite blocks, as a consequence, the additional free space in which vanadium ion can move resulting in a polarizability increase and with a rise of dielectric permittivity level.

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It should be also mentioned that in case of the SBN and SBT ceramics the doping of vanadium causes a shift in the phase transition temperature to a higher value [7,8].

The replacement of Sr with Ba ions (BBN) in mentioned ceramics caused structural disorder, which is responsible for significant broadening of the temperature dependence of real part of permittivity [9–11] and also appearing properties characteristic for ferroelectric relaxors. The structural investigations of $ABi_2Nb_2O_9$ (A = Ba, Sr, Ca) carried out by Blake et al. [12] revealed, that the origin of mentioned disorder is connected with the antiside defects of Bi^{+3} and A^{2+} cations, which concentration increased with the increasing A cation size.

In light of the presented literature, replacement of niobium ions with vanadium ions in $BaBi_2Nb_2O_9$ ceramics should lead to a decrease of the packing degree of ions in lattice unit cell and facilitate the proper incorporation of the barium ions in the lattice. As a consequence the number of the antiside defects should decrease and the relaxor properties of the BBN ceramics should be weaker.

The results of the investigation into the influence of vanadium admixture on the value of the lattice parameter as well as the dielectric properties confirm those assumptions, which is extensively described in the paper.

2. Experiment

The vanadium doped BBN ceramic was obtained by a conventional solid-state reaction of thermal sintering of all compounds, oxides and carbonates. Based on the above-mentioned literature, the following dopant amounts were chosen: 1; 5 and 10 at% Stoichiometric quantity of $BaCO_3$, Bi_2O_3, Nb_2O_5 and V_2O_5 reagents were weighed and blended for 24 h. The mixture was pressed into cylindrical pellets and placed in a closer, double crucible. The calcination process was carried out at a temperature of 950 °C for 2 h. Then the materials were ground using the mixer mill (Retsch MM200) for 24 h. The dry powder was sieved, mixed for 12 h and pressed in the form of cylinders and again placed in a double crucible. The second, final thermal sintering was at 1050 °C for 3 h. As a result, the obtained BBN ceramics have a 98% density as compared to the theoretical ones.

The microstructure of the discussed material and the distribution of all elements throughout the grains were examined by the scanning electron microscope (SEM), JSM-5410, with an energy dispersion X-ray spectrometer (EDS) by Oxford Instruments. The measurements were performed on the fractured surface of ceramics.

XRD measurements were carried out on powdered samples using a Huber diffractometer with monochromatic CuKα1 radiation (30 kV, 30 mA). The angle scale of the received diffraction diagrams was scaled to 2θ (Bragg-Brentano geometry) by Au standard (JCPDS number 12-0403). The diagrams were measured from 20 to 100° in 2θ with 0.05° steps.

All the ceramic samples destined for electric measurements were polished to obtain flat and parallel surfaces. The thickness of samples for electric measurements was about 0.6 mm. The samples were coated with silver electrodes using an appropriate silver paste, without thermal treatment and deaged at 500 °C for 10 min prior to measurements. The measurements of permittivity (ε') as a function of temperature and frequency of the measuring field were carried out using an automatic measuring system with HP 4192A impedance analyzer. Whereas the thermally stimulated depolarization currents (TSDC) were measured using the computerized measuring system with the picoamperometer Keithley 6485, which was crucial part.

3. Results and discussion

The scanning electron micrographs for ceramics without vanadium as well as with 5 and 10 at% are shown in Fig. 1.

An analysis of all obtained images indicate that together with the change of vanadium concentration from 0 to 10 at% the average grain size increased by 2 μm. These results are in agreement with the conclusions stated by authors [13], concerning the SBN ceramics modified by vanadium. It should be marked that the shape of grain transformed from oval to plate lamella pattern (Fig. 1b).

An energy dispersion X-ray spectrometer was used to check the distribution of individual elements within the grains. Microanalysis was performed with the ISIS-300 SEMQuant program. The quantitative analysis takes into account the content of barium, bismuth, and niobium, oxygen was omitted. The reason for omitting the oxygen was the anxiety of adulteration the results caused by the excess oxygen presented in pores and originating from the atmosphere. The content of the investigated elements was normalized to 100% (Table 1). The results presented in Table 1 strongly confirm that the measured elements concentration, within the range of measurement error (equal to1 at% for EDS analysis), only slightly differ from the theoretical values.

The X-ray diffraction patterns (XRD) of BBN ceramics with 1, 5 and 10 at% of vanadium content obtained at room temperature are shown in Fig. 2. The results indicate the formation of monophasic vanadium-doped $BaBi_2Nb_2O_9$ structure for all considered amount of dopant, whereas the previous studies [3] of BBN ceramics have shown that the system prevents monophasic up to 5 at% of vanadium. The differences are likely a consequence of sample preparations. In case of the samples described in the article considerable attention has been paid to long-term mixing and grinding powders both before first and second sintering.

The pure and vanadium dopant ceramics are characterized by tetragonal structure with space group I4/mmm[12,14]. The lattice parameters obtained from X-ray patterns are presented in Fig. 3. The change in the linear character of the lattice parameters show that the Vegard rule is fulfilled, which means that the vanadium ions are

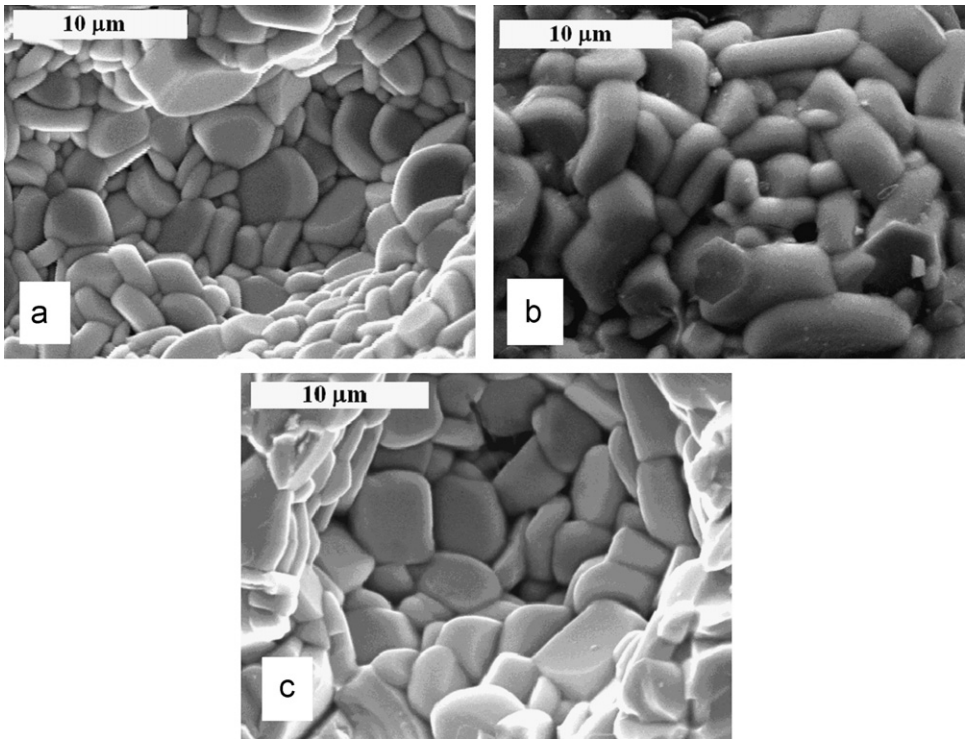

Fig. 1. SEM image of the pure $BaBi_2Nb_2O_9$ ceramics (a) doped with 5 at% (b) and 10 at% (c) of vanadium.

Table 1
The elements content in V doped $BaBi_2Nb_2O_9$ ceramics.

Composition	Stoichiometry	Ba [%]	Bi [%]	Nb [%]	V [%]
$BaBi_2Nb_2O_9$+1 at%V	theoretical	20	40	39.6	0.4
	real	20	39	40	0
$BaBi_2Nb_2O_9$+5 at%V	theoretical	20	40	38	2
	real	21	39	38	2
$BaBi_2Nb_2O_9$+10 at%V	theoretical	20	40	36	4
	real	20	40	36	4

statistically distributed in the bulk of sample and the obtained ceramics are only single phase [15,16].

Taking into account the difference in the ionic radius of vanadium and niobium ions one would expect significant changes in the size of the lattice parameter. In fact, the observed changes were much smaller, which points to a shrinking process of the unit cell, connected with the small value of vanadium ions, which is restrained by the $(Bi_2O_2)^{2+}$ layers [6]. The free space, which is created in the lattice unit cell, is conducive to the proper incorporation of the barium ions. The increase in the grain size has also plays role. Namely in the case of the pure BBN ceramics the bigger the grain size permit the more barium ions properly enter in the crystal lattice [17]. The correct entering of barium ions leads to a decrease in the number of defects. Namely when the Bi^{3+} cations exchange Ba^{2+} donor centers in the perovskite layers and acceptor centers in Bi_2O_2, slabs are formed. Such centers should be self-compensating in isotropic structures unlike those in layered structures. Thus acceptor centers in bismuth layers are at least partly compensated by oxygen vacancies whereas donor centers in perovskite layers are compensed by electron or cation vacancies [18,19].

Results of dielectric investigations as well as the investigations of temperature dependence of thermally stimulated depolarization currents (TSDC) confirm the assumption.

The dielectric measurements were done using an Agilent 4294A Precision Impedance Analyzer. The dielectric permittivity as a function of temperature measured with a frequency measuring field equal to 100 kHz is presented in Fig. 4a, whereas Fig. 4b illustrates the changes of temperature T_m (corresponding to the maximum of real part of dielectric permittivity), which moved to higher value with the increasing of vanadium dopant.

The above-mentioned insignificant changes of lattice parameters in connection with the small ionic radius of

vanadium atoms (in comparison with ones of niobium) lead to an increase of the polarizability, which resulted in a gradual increase of the dielectric permittivity value.

All dependencies presented in Fig. 4a show a strong diffusive character. Moreover, deviations from Curie-Weiss law are observed in the range of the paraelectric phase (Fig. 5a) and can be described by the parameter γ in the formula:

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_{\max}} = \frac{C}{(T - T_{\max})^{\gamma}}$$

The origin of this behavior is connected with inhomogeneous distribution of barium ions and local charge imbalance in the layered structure. Namely, the Ba ions are entering not only the perovskite blocks but also $(Bi_2O_2)^{2+}$ layers. In the case of the investigated ceramics the coefficient γ decreases with the increase of vanadium content (Fig. 5b), which points to the disappearance of defects. The results agree with the previous assumptions concerning the proper incorporation of barium ions to the crystal lattice, connected not only with the smaller ionic radius of vanadium, but also with the increasing size of grains [17]. Such incorporation lead to the decrease in the number of donor centers in perovskite layers and acceptor centers in Bi_2O_2 as well as oxygen and cation vacancies [18,19]. The crystal structure is ordered.

All the discussed ceramics are characterized by typical properties for ferroelectric relaxors, specifically frequency dispersion of maximum value of real part of dielectric permittivity and temperature T_m (Fig. 6). The degree of dispersion of ε'_{max} and T_m, understood as $\Delta\varepsilon'_{max} = \varepsilon'_{max}$

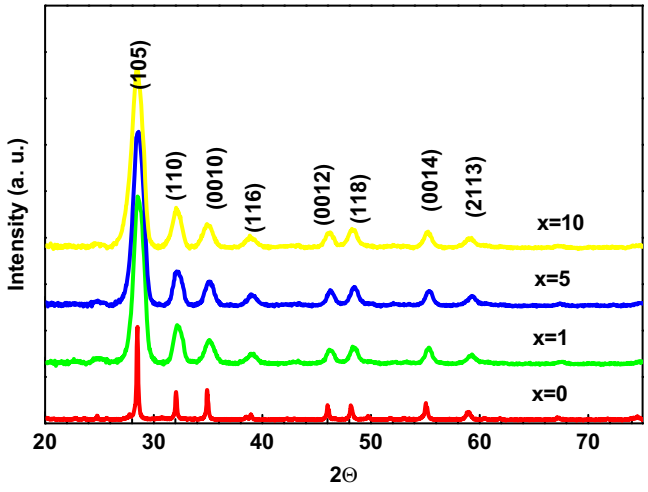

Fig. 2. XRD pattern of BBN ceramics with 0, 1, 5 and 10 at% of vanadium content.

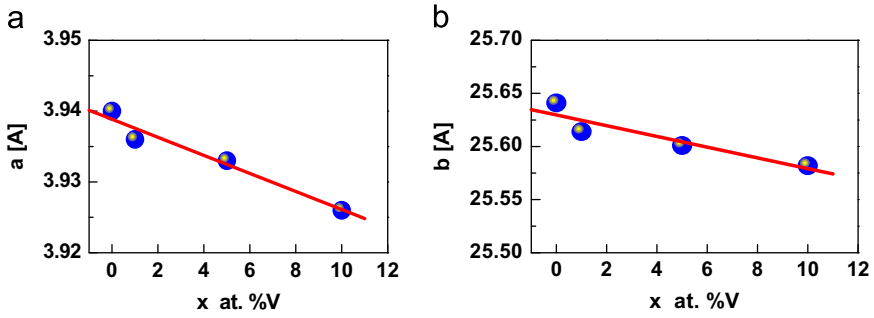

Fig. 3. The lattice parameters of vanadium doped $BaBi_2Nb_2O_9$ ceramics.

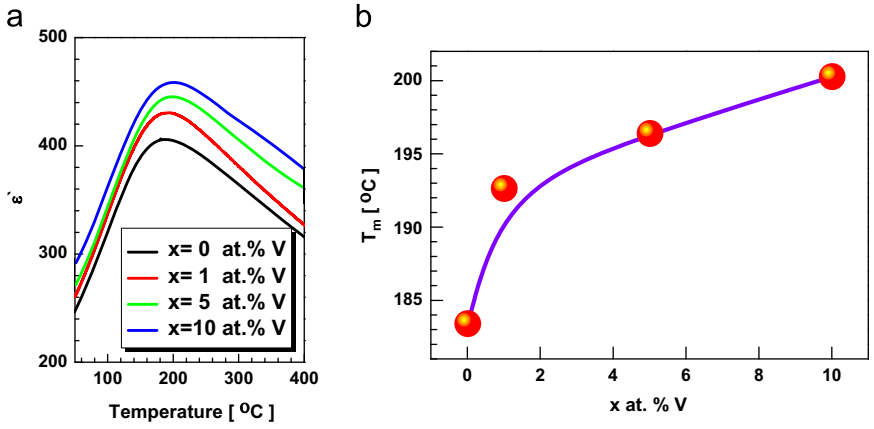

Fig. 4. The dielectric permittivity as a function of temperature measured by heating at frequencies equal to 10 kHz (a) and dependence of temperature T_m corresponding to ε_{max} on the V concentration (b).

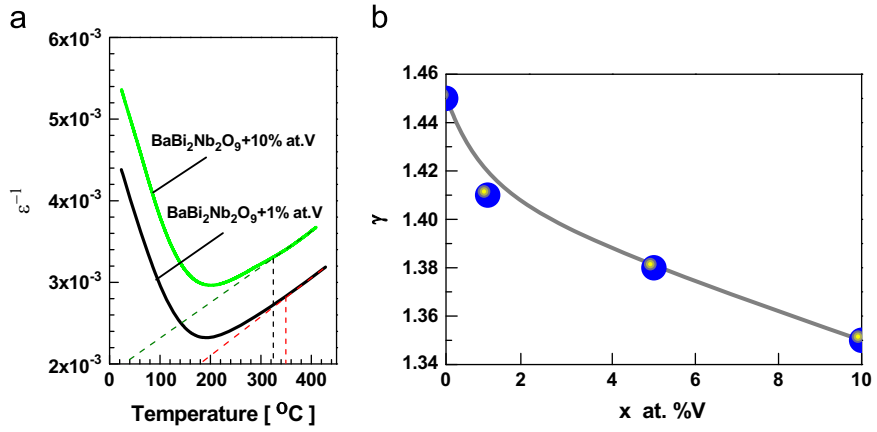

Fig. 5. The inverse of dielectric permittivity for undoped and V modified ceramics (a) and broadening parameter vs. vanadium concentration (b).

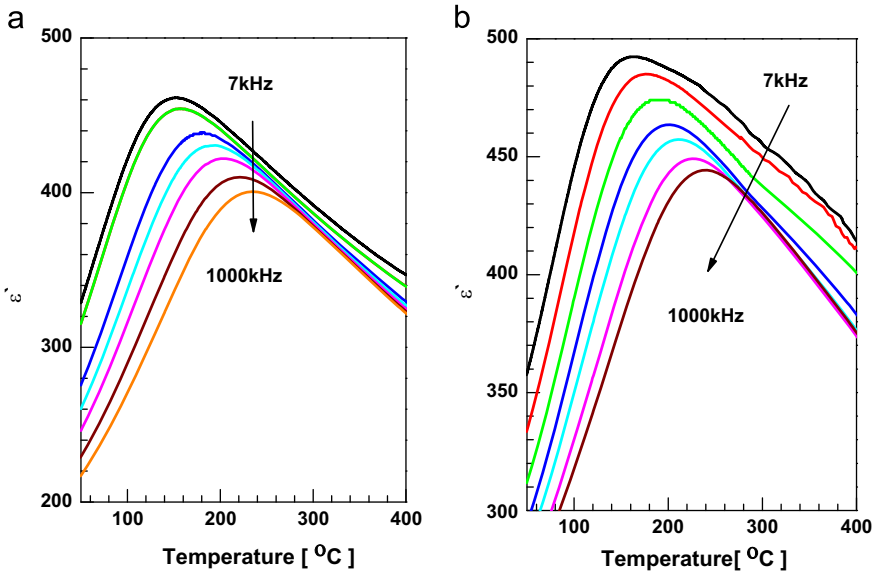

Fig. 6. Dielectric permittivity as a function of temperature measured by heating at various frequencies, for (a) 1 at% and 10% (b) vanadium modified BBN ceramics.

(500 Hz) $-\varepsilon'_{max}$(1 MHz) and $\Delta T_m = T_m$(1 MHz) $- T_m$(500 Hz), decreases together with the growth of dopant concentration

The frequency dependence of temperature of maximum dielectric permittivity (T_m) can be described by Vogel-Fulcher equation:

$$f = f_0 \exp\left[\frac{-E_a}{k(T_m - T_f)}\right] \quad (1)$$

where E_a is the activation energy, T_f is the freezing temperature of polarization fluctuation, and f_o is the pre-exponential factor. The values of T_f, f_o and E_a calculated from the above relationship versus the content of the vanadium admixture are collected in Table 2.

Replacement of the niobium ion by much smaller vanadium one caused the reduction of the activation energy value and an increase of freezing temperature. This fact is in agreement with the conclusion drawn above: the vanadium ions due to their small ionic radius caused the order of the crystal structure and made it easier to incorporate the barium ions to the correct location- in the perovskite blocks. It is lead to decrease the properties characteristic for ferroelectric relaxor.

Table 2
Parameters T_f, E_a and f_o determined from Vogel-Fulcher relationship.

x (at%) of vanadium	E_a (eV)	T_f (°C)	f_o (Hz)
0	0.46	−103	9.68×10^{12}
1	0.41	−78	1.14×10^{12}
5	0.36	−53	1.06×10^{12}
10	0.34	−41	1.92×10^{12}

The correct location of barium ions in a crystal structure should be connected with the decrease of space charge participation. To confirm the theory, the measurements of

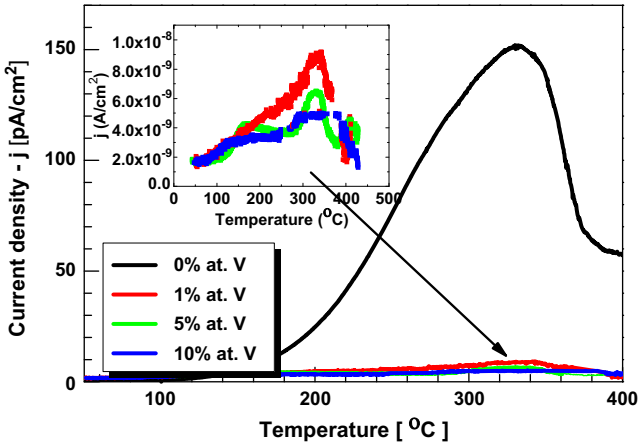

Fig. 7. The thermal stimulated depolarization current versus temperature for undoped and vanadium modified BBN ceramics pre-polarized by applying electric field of 1 kV/cm at constant temperature 200 °C.

thermal stimulated depolarization currents were done. The sample was first polarized at dc field with strength 1 kV/cm applied for 10 min.at temperature 200 °C and then cooled in the field to 0 °C at which the field was switched off. The samples were heated with a constant rate of 5 K/min to the temperature 450 °C. The temperature changes of the observed thermally stimulated depolarization currents (TSDC) are shown in Fig. 7. In the case of pure BBN ceramics on the presented characteristic, the distinct broadened maximum appeared at a temperature higher than the temperature at which the ceramics were pre-polarized. The shift in these maximum results from a mutual interaction of orientation (dipole) part of metastable polarization and the polarization of the free ion and electron space charges, participating in the screening process of the polar-region, which was widely discussed in papers [10,20]. The TSDC density decreased drastically by almost two orders of magnitude from maximal value 1.5×10^{-7} A/cm^2 for pure BBN, to 8.5×10^{-9} A/cm^2 for 1 at% vanadium content. Further increases of vanadium concentration caused a gradual decrease in the final lack of this current in the case of 10 at% vanadium content. These results indicated a dramatic drop of space charge in the volume of the sample. Apparently the homovalent admixture of vanadium due to its small ionic radius, as well as the increasing size of grains [17], which favours proper incorporation of individual ions in the crystal lattice and lead to the decreased number of defects. It is only an assumption, which opened the way for the following investigations, in particular the detailed structural studies.

4. Conclusions

The admixture of vanadium ions to BBN ceramics has an influence on the size and shape of grains. Taking under consideration the ionic radius of vanadium the changes in the lattice parameters should be expected. However the XRD measurements show that the parameters do not change, which implies that the ordering of the crystal structure and the decrease in the number of defects takes place. Namely the incorporation of a smaller vanadium ion in place of niobium without any changes to lattice parameters have an influence on the proper entering of the barium ions into the perovskite blocks instead off the $(Bi_2O_2)^{2+}$ layers, which favours the weakening of the relaxor properties. The weakened properties are reflected in a considerable reduction in the frequency dispersion of the maximum value of electric permittivity and temperature T_m and also in the increasing of activation energy. The assumptions were considered by the results of the thermally stimulated depolarization current density measurements. The maximum value of the TSD current decreased significantly with the increase of the vanadium admixture, which points to the decrease of the space charge participation in samples.

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