

A.V. Gaponov, O.V. Vorobiov, A.M. Vasyliiev

Electrical Parameters of SnO₂ Based Varistor Ceramics with CaO and BaO Additions

*Oles' Gonchar Dnipropetrovs'k National University, 72 Gagarin Ave., Dnipropetrovs'k, 49010,
Ukraine, e-mail: alexei_gaponov@ukr.net*

In the tested SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO varistor ceramics the adding of CaO or BaO oxides leads to the decrease of the electric conductivity in the low electric field and correlated increase of the potential barrier height at the SnO₂ grain boundaries (from 0.7 to 1.0 eV). The coordinated changes of electrical parameters with the increase of the burning temperature from 1520 to 1620 K (the increase of the linear shrinkage, a grain size, an electric conductivity, a nonlinear coefficient b , a normalized nonlinear coefficient b_E , a dielectric permittivity and the decrease of the qualifying electric field E_1 , an activation energy of electric conduction and a grain specific resistance) prove the barrier mechanism of electric conductivity in the SnO₂ based ceramics. The highest data $b = 58$ and $b_E = 0.02 \text{ cm} \cdot \text{V}^{-1}$ has ceramics with CaO addition baked at 1620 K. According to the impulse experimental data in the high electric field the increase of burning temperature causes the increase of SnO₂ grain average size and the decrease of their grain specific resistance r_g . The obtained value $r_g = 1.1 \text{ Ohm} \cdot \text{cm}$ for SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO ceramics is the lowest among those found in SnO₂ based ceramics. The addition of CaO or BaO increase the grain specific resistance and decrease their average size.

Key words: varistor, SnO₂, ceramics, grain boundary, CaO, BaO, electric conductivity, specific resistance, grain size.

Стаття постуила до редакції 30.08.2015 ; прийнята до друку 15.12.2015.

Introduction

Along with the widespread ZnO based ceramics applied for the overvoltage protection [1, 2] the SnO₂ based ceramics which can be used as a varistor material has intensively been investigated for the last two decades. SnO₂ based ceramics was found earlier [3]. It is characterized by the high nonlinearity of the voltage current characteristics [4-10]. Such ceramics has nonohmic electric conductivity which is caused by the potential barriers at the SnO₂ grain boundaries. The model of tin dioxide varistors assumes that the grain-boundary barriers are the double Schottky barriers (two Schottky barriers connected in opposite directions). These barriers are decreased with the increase of the voltage applied to the samples [7-10].

As voltage protective elements the varistors work in the impulse mode [11-17]. The characterization of the samples under impulse influence when the grain boundary resistance is close to the grain resistance is an important precondition for the creation of the high-quality varistors. Hence, the study of voltage current characteristics of the ceramics not only in low currents

10^{-8} - $10^{-1} \text{ A} \cdot \text{cm}^{-2}$ (these ones are described in many scientific works, for example [4-8]) but also in high currents 10^1 - $10^3 \text{ A} \cdot \text{cm}^{-2}$ are of great interest nowadays.

We have already investigated SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO varistor ceramics with alkaline-oxide metal additions CaO, SrO and BaO [18]. Tin dioxide is characterized by low densification during sintering (which is controlled by the evaporation-condensation mechanism [4]) due to its high vapour pressure at higher temperatures. In order to enhance density in the studied ceramics, Co₃O₄ is added. This oxide causes modifications in the oxygen vacancy concentration and promotes an increase in density of the ceramics [19]. At high temperatures, Co₃O₄ decomposes into CoO and Co₂O₃ [20]. Consequently, cobalt can exhibit both Co²⁺ and Co³⁺ oxidation states. The substitution of the Sn⁴⁺ ions by Co²⁺ and/or Co³⁺ leads to the formation of oxygen vacancies and can explain the high densification of ceramic materials.

The addition of Nb⁵⁺ in small amounts to the SnO₂ ceramics results in the electron concentration increase, which enhances the electronic conductivity in the SnO₂ lattice and leads to the higher conductivity of grains [21].

The addition of Cr_2O_3 into the SnO_2 lattice results in the substitution of Sn^{4+} by Cr^{3+} . The addition of Cr_2O_3 gives the more homogeneous microstructure of materials and the higher nonlinearity of voltage current characteristics [4].

The addition of CuO forms a liquid phase during the sintering process and enhances the sintering rate of ceramics [20]. At high temperatures (above 1300 K) in the Cu-based phase ions Cu^{2+} and Cu^+ appear [22]. After cooling the layers of Cu-riched phase cover the SnO_2 grains [23]. The thickness of Cu-riched intergranular phase is several nanometers. The liquid phase which exists during ceramics baking can improve the distribution of Cr_2O_3 throughout the sample and as a result enables to create high potential barriers on the SnO_2 grain boundaries. Then the low-field conductivity becomes lower [23].

The addition of CaO and BaO results in the segregation of ions with large ion radius Ca^{2+} (104 pm) or Ba^{2+} (138 pm) on the grain boundaries [18]. It enables to create the higher potential barriers on the grain boundaries of ceramics. The addition of SrO increases the qualifying electric field E_1 [18] which is defined at current density of $1 \text{ mA}\cdot\text{cm}^{-2}$. Therefore in the further experiments only the materials with CaO or BaO additions will preferably be used.

The burning temperature is the factor which influences the characteristics and parameters of baked samples [8, 24]. The increase of burning temperature from 1375 to 1675 K causes the increase of grain size, electric conductivity and dielectric permittivity and the decrease of electric field E_1 and activation energy of electric conduction [24]. The largest values of nonlinear coefficient $b = (E/j)(dj/dE)$ have the ceramics baked at 1525 K but the largest values of the normalized nonlinear coefficient $b_E = b/E_1$ [7, 24] have the ceramics baked at 1600 K.

While testing different characteristics of SnO_2 based ceramics a special attention should be paid to the correlation of a great number of electrical parameters which influence the varistor properties of the obtained materials. Hence the aim of this work is to investigate the electrical parameters of $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3\text{-CuO}$ ceramics with CaO or BaO additions baked at 1520 and 1620 K in the wide range of current densities $10^8\text{-}10^3 \text{ A}\cdot\text{cm}^{-2}$.

I. Experimental details

The composition of ceramics (mol. %) (98.9- x) SnO_2 - 0.5 Co_3O_4 - 0.05 Nb_2O_5 - 0.05 Cr_2O_3 - 0.5 CuO - $x\text{ACO}_3$ ($x = 0$ or 0.5 mol. %, $A = \text{Ca}$ or Ba) was mixed with the addition of distilled water. After drying it was pressed into disks of 12 mm diameter and thickness approximately 0.9 mm under the axial pressure of 45 MPa. The pressed disks were heated with the speed of 300 K/h up to 1520 or 1620 K, kept at this temperature during 1 hour and cooled in the switched off furnace to the room temperature. While heating the decomposition of carbonates CaCO_3 or BaCO_3 with CO_2 emission took

place and these compounds changed into CaO or BaO [18].

The shrinkage of the samples g was calculated by the formula $g = (D_0 - D) \cdot D_0^{-1}$ where D_0 and D are the diameters of the sample before and after burning. The microstructure of ceramics was studied by the scanning electron microscopy Zeiss Supra 35VP.

After baking the samples were kept for a long time in the room conditions in order to achieve the stability of their electrical properties because during the first 6 months after burning the gradual evolution of electrical parameters took place [25]. Silver was used as electrode material. Silver-containing paste was applied to the plane-parallel surfaces of the samples which were slowly heated up to 1070 K with further cooling till the room temperature in the switched off furnace. The electrical measurements were made in a certain period of time after preparing the electrodes. It was required to achieve the stability of electrical characteristics of ceramics [25].

The voltage current characteristics in low currents were registered by applying the direct voltage and the measurement of the constant values of current. The possible sample self-heating which is peculiar to the SnO_2 based ceramics [9, 10, 23-26] is determined as the increase of current at fixed voltage. The results were registered avoiding the Joule heating of ceramics. The nonlinear coefficient $b = (E/j)(dj/dE)$ is estimated at the current density of $j = 10^{-3} \text{ A}\cdot\text{cm}^{-2}$. The qualifying electric field E_1 is evaluated at the same current density.

The activation energy of electric conduction of ceramics E_S was determined from the temperature dependence of electric conductivity in low electric fields, using the formula $S = S_0 \exp(-E_S/kT)$, where S_0 is a constant, k is the Boltzmann's constant, T is the absolute temperature.

In order to test the current voltage characteristics in high current field the single impulses with front approximately 8 μs and slow slope (for approximately 20 μs from the impulse beginning the current fell down up to the half of the amplitude) were given to the samples. So called 8/20 impulses are used during the testing of impulse impact on the varistors [11-18]. The interval between the impulses was 5 min. The oscillograms of voltage and current through the sample were registered with the help of storage oscilloscope C8-11. To build up the voltage current characteristics which were measured on the impulses the peak values of voltage and current were used.

The SnO_2 grain specific resistance and their average size were estimated using voltage current characteristics in high current range $j = 10^1\text{-}10^3 \text{ A}\cdot\text{cm}^{-2}$. With these values j specific resistance was calculated from the linear part slope of dependence built in coordinates $E \sim j$, using the formula $r_g = \Delta E/\Delta j$ [11-13], where ΔE is the growth of the electric field and Δj is the growth of the current density. In order to evaluate the grain average size l_g the linear part of voltage current characteristics

Table 1

Some parameters of SnO ₂ -Co ₃ O ₄ -Nb ₂ O ₅ -Cr ₂ O ₃ -CuO ceramics with CaO or BaO additions								
Addition	Linear shrinkage g , %	Grain average size l_g micr, μm	Nonlinear coefficient b	Electric field E_1 , $\text{V}\cdot\text{cm}^{-1}$	Normalized nonlinear coefficient $b_E = b/E_1$, $\text{cm}\cdot\text{V}^{-1}$	Activation energy of electric conduction E_G , eV	Electric conductivity S , $\text{Ohm}^{-1}\cdot\text{cm}^{-1}$	Dielectric permittivity ε (1 kHz)
Baked temperature 1520 K								
–	10.9	6.2	37	2980	0.0124	0.66	$7.1\cdot 10^{-11}$	2147
CaO	10.6	3.8	42	7300	0.0058	0.86	$9.2\cdot 10^{-12}$	230
BaO	9.6	3.7	30	8160	0.0037	1.01	$5.2\cdot 10^{-12}$	253
Baked temperature 1620 K								
–	11.8	9.3	26	1860	0.0140	0.64	$2.4\cdot 10^{-10}$	4123
CaO	11.3	6.9	58	2960	0.0196	0.85	$6.4\cdot 10^{-11}$	1544
BaO	10.0	6.7	33	3880	0.0085	0.88	$3.6\cdot 10^{-11}$	1064

in high current field was extrapolated to the crossing with electric field axis. The obtained value E_0 was used to find l_g with the formula $l_g = E_g/E_0$ [11-13], where $E_g \approx 3.6$ eV is the width of SnO₂ energy gap [27].

The AC capacity C was measured at the 1 kHz frequency by LCRG measuring device Tesla BM 591. The dielectric permittivity of the ceramics was calculated with the formula $\varepsilon = Ch/(e_0S)$, where h is the sample thickness, S is the electrode area and e_0 is a dielectric constant.

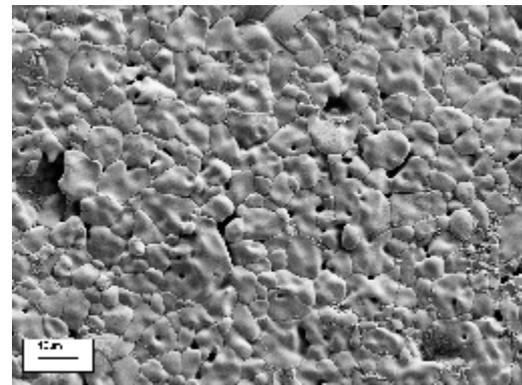
II. Results and discussion

The small additions in SnO₂ can change the barrier formation conditions and, therefore, it can change electrical properties of SnO₂ varistors. The barrier formation process in SnO₂ varistor ceramics can be influenced by the grain-boundary phase formation.

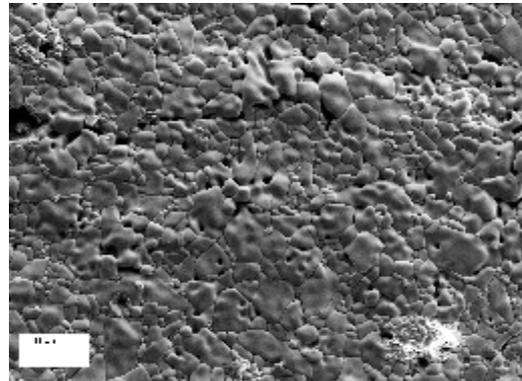
In order to test the ceramics microstructure the surface microphotographs of the samples baked at 1520 K were presented in *fig. 1*. Cu-rich intergranular phases which were in liquid state during the burning cover SnO₂ grains in SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO ceramics (*fig. 1, a*). This Cu-rich phase occurs at grain boundaries rather inhomogeneously throughout the sample. The situation can be quite complicated due to possible conversion of CuO to Cu₂O in the process of synthesis [22].

Cu-riched intergranular phases are almost undetectable while adding CaO or BaO (*fig. 1, b and c*). It can be connected with Ca²⁺ or Ba²⁺ ion segregation with large ion radius (104 pm and 138 pm respectively) on the grain boundaries (Sn⁴⁺ ion radius is 67 pm). CaO or BaO interrelate with Cu-riched phase [18] and therefore it is almost impossible to find this phase on the grain boundaries.

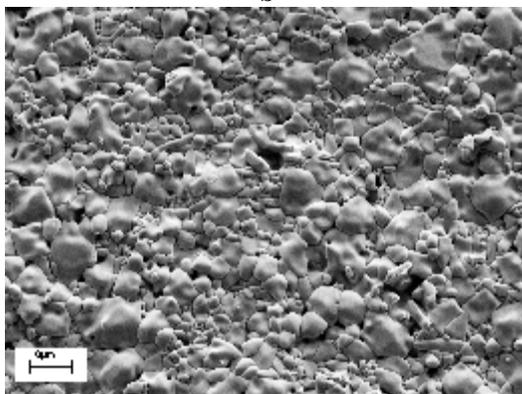
The grain average size of SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO ceramics baked at 1520 K is 6.2 μm (*tab. 1*) and quite the great number of pores are observed in a sample (*fig. 1, a*). Such ceramics has a linear shrinkage of $g = 10.9$ %. While adding CaO or BaO the shrinkage of



a



b



c

Fig. 1. SEM micrographs of the as-sintered surface of SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO varistor ceramics without (a) and including of CaO (2) or BaO (3) additions baked at 1520 K.

samples decreases up to 10.6 or 9.6 % correspondingly and at the same time a grain average size decreases (*tab. 1*). It is probably connected with worsening of synthesis due to the ions with large ion radius and the emergence of the unfavourable conditions for SnO₂ grain growth.

When the burning temperature increases up to 1620 K the grains in three tested systems of ceramics grow greater and the shrinkage of the samples increases (*tab. 1*). The microstructure of such materials [18] is similar to the microstructure of corresponding samples baked at 1520 K. The increase of burning temperature leads to the formation of the more solid and less porous structure of varistors.

The dependences of current density on electric field for SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO ceramics with CaO or BaO additions are presented in *fig. 2*. The observed varistor properties can be explained in the frames of grain-boundary double Schottky barrier concept as a decrease of the barrier height with the increase of electric field.

The electric conductivity of ceramics S is connected with potential barrier height j_0 on the grain boundaries:

$S = S_0 \exp(-j_0 + h)/kT) = S_0 \exp(-E_S / kT)$, where h is the distance of Fermi level from the bottom of conduction band in the grain depth. In tin dioxide based varistor ceramics the Fermi level far from the SnO₂ grain boundary is located below the conduction band edge at about 0.1-0.2 eV [27]. Therefore, the barrier height j_0 is only slightly less than the activation energy of electrical conduction E_S which was evaluated with temperature dependence of electric conductivity (*fig. 3*) in high-temperature area. As a result, the obtained E_S values in SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO samples give quite correct estimation of the barrier height: $j_0 \cong E_S \cong 0.65 \text{ eV}$ (*tab. 1*).

With adding CaO or BaO in SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO ceramics the activation energy increases which leads to the decrease of electric conductivity in low electric field (*tab. 1*). With larger burning temperature the activation energy is somewhat less therefore the corresponding values of electric conductivity in low electric field are larger. It means that in the SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO ceramics and in the ceramics with CaO or BaO additions conduction is controlled by the grain-boundary barriers.

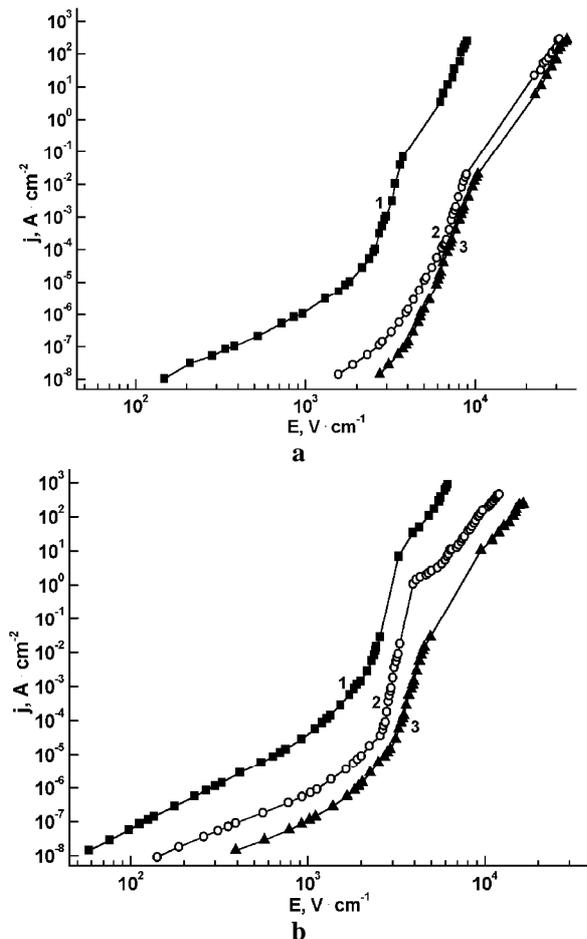


Fig. 2. Current density vs. electric field in SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO varistor ceramics without (1) and with CaO (2) or BaO (3) additions baked at 1520 K (a) and 1620 K (b).

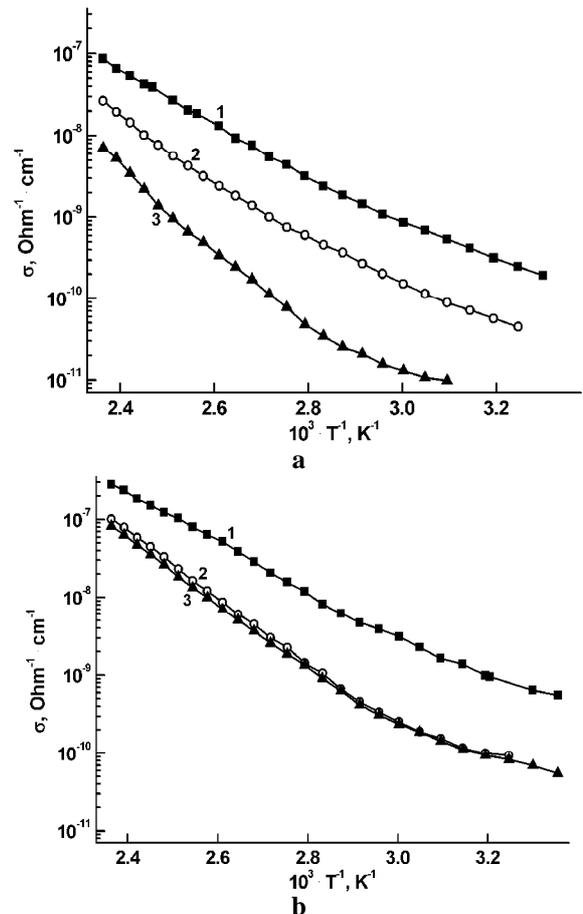


Fig. 3. Temperature dependences of DC low-field electric conductivity for SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO varistor ceramics without (1) and with CaO (2) or BaO (3) additions baked at 1520 K (a) and 1620 K (b).

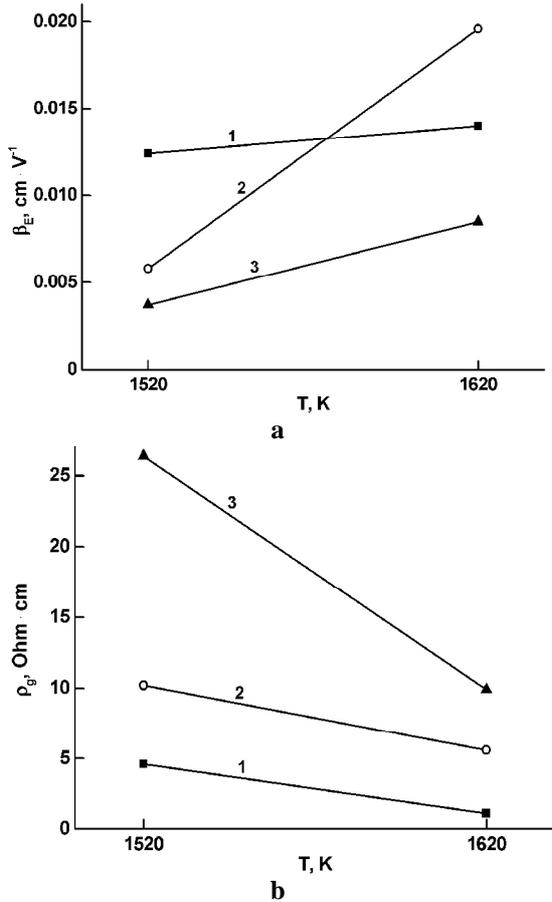


Fig. 4. Dependences of the normalized nonlinear coefficient (a) and grain specific resistance (b) on baked temperatures for SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO varistor ceramics without (1) and with CaO (2) or BaO (3) additions.

It is necessary to point out that SnO₂ grain structure, mutual orientation of neighboring grains, surface structure of SnO₂ grains, surface electronic structure, chemisorbed oxygen, used oxide additives and other factors determine the conditions for barrier formation during sintering in oxidizing atmosphere. This problem is quite complicated (see, for example, [27]) and, extends beyond the composition analysis discussed in this paper. On that reason the structure of grains and grain boundaries are not discussed in this paper.

The values of the qualifying electric field E_1 in SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO ceramics obtained during the experiments (*tab. 1*) are not too high (about $(2 - 3) \cdot 10^3 \text{ V} \cdot \text{cm}^{-1}$). These values increases with CaO addition and even more increases with BaO addition in samples obtained at both burning temperatures (*fig. 2*). The increase of E_1 is connected with the decrease of grain average size. The burning at larger temperature leads to the grain growth of the ceramics and less corresponding values of E_1 (*tab. 1*).

The values of dielectric permittivity of the samples ϵ are also specified by SnO₂ grain sizes: the less they are the less value of ϵ we have (*tab. 1*). Somewhat larger values of ϵ with BaO addition than those with CaO addition in the samples baked at 1520 K is

connected with close values of grain average size in such ceramics and, possibly, with some large grains in sample volume. Such grains were not taken into consideration while determining the grain average size at its surface. In this case the cross-section between large grains is significant and the number of in-series capacities of separate grain boundaries is less. Therefore the value of dielectric permittivity is somewhat larger (*tab. 1*).

In baked at 1520 K ceramics with CaO addition the nonlinear coefficient increases from 37 to 42 and in the same ceramics baked at larger burning temperature 1620 K it increases from 26 to 58 (*tab. 1*). The growth of voltage current characteristics nonlinearity takes place due to the quick decrease of potential barrier height on the grain boundaries at the quite great values of electric field [9] in the system with CaO addition. Baked at 1620 K ceramics with CaO addition has the largest value $b = 58$ at not too high electric field ($E_1 = 2960 \text{ V} \cdot \text{cm}^{-1}$). It allows to use this ceramics in commercial conditions. The value $b = 26$ is quite little for basic ceramics baked at 1620 K which is explained by the calculation of nonlinear coefficient at current density of $10^{-3} \text{ A} \cdot \text{cm}^{-2}$ (*fig. 2, b*), when the voltage at the sample was still not enough to achieve high nonlinear area at voltage current characteristics. The BaO addition does not cause the increase of nonlinear coefficient (*tab. 1*) possibly due to the gradual decrease of the potential barrier height on the grain boundaries at quite large electric fields.

The normalized nonlinear coefficient $b_E = b / E_1$ decreases in baked at 1520 K ceramics with CaO addition and even more decreases with BaO addition (*fig. 4, a*). It takes place due to the large values of E_1 in such samples (*tab. 1*). In baked at larger burning temperature 1620 K ceramics the corresponding values of E_1 are almost two times as less as those of the ceramics baked at 1520 K. Hence the corresponding values of b_E will be larger (*fig. 4, a*). The largest normalized nonlinear coefficient $b_E = 0.02 \text{ cm} \cdot \text{V}^{-1}$ has SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO ceramics with CaO addition baked at 1620 K. It is caused by a large nonlinear coefficient b at quite a moderate qualifying electric field E_1 . The obtained value of $b_E = 0.02 \text{ cm} \cdot \text{V}^{-1}$ is among the largest ones for the samples of SnO₂ ceramics [7, 24].

At high electric currents $j = 10^1 - 10^3 \text{ A} \cdot \text{cm}^{-2}$ the potential barrier height on the grain boundaries decreases and the electric conductivity of ceramics is controlled both by low potential barriers and relatively conductive SnO₂ grains [14-18]. The evaluated with voltage current characteristics in high current densities (approx. up to $1000 \text{ A} \cdot \text{cm}^{-2}$) the grain average size in ceramics baked at 1520 K decreases with CaO or BaO additions from 4.5 to 1.3 μm and in ceramics baked at 1620 K from 6.8 to 3.7 and 2.6 μm correspondingly (*tab. 2*). The decrease of grain average size correlates with the data obtained by electron scanning microscope. Possibly, the presence in ceramics the elements with large ion radius, as it was mentioned above, worsens the baking of ceramics. As a result the grains of such ceramics grow less.

Table 2Grain specific resistance and grain average size obtained of pulse regime and of scanning electron microscopy for SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO ceramics with CaO or BaO additions

Addition	Grain specific resistance ρ_g , Ohm·cm	Grain average size (pulse regime) $l_{g \text{ pulse}}$, μm	Grain average size (scanning electron microscopy) $l_{g \text{ micr}}$, μm
Baked temperature 1520 K			
–	4.6	4.5	6.2
CaO	10.2	1.3	3.8
BaO	26.4	1.3	3.7
Baked temperature 1620 K			
–	1.1	6.8	9.3
CaO	5.6	3.7	6.9
BaO	9.9	2.6	6.7

It should be noted that all values of grain average size calculated with the help of impulse testing are less than those obtained by electron microscopy (*tab. 2*). It can be explained by more rapid grain growth on the surface of samples in direct contact with environment during burning. Within the samples there are the grains of less size which influence upon grain total average size calculated with voltage current characteristics at high currents. The increase of burning temperature on 100 K fosters the larger grain growth and it is resulted into larger grain sizes (*tab. 2*).

The SnO₂ grain specific resistance in the samples baked at 1520 K increases with CaO or BaO additions from 4.6 to 10.2 and 26.4 Ohm·cm correspondingly (*tab. 2*). Adding to the ceramics CaO or BaO with large ion radius elements (104 pm and 138 pm respectively) leads to their segregation on grain boundaries and the increase of grain specific resistance. The increase of burning temperature on 100 K causes the decrease of grain specific resistance in 2-4 times up to 1.1, 5.6 and 9.9 Ohm·cm (*fig. 4, b*). The larger burning temperature fosters both the increase of grain cross section and, possibly, the better spread of Nb₂O₅ (it is responsible for electric conductivity of grains) in presence of CuO based phase which is liquid during the burning [23]. Therefore the improvement of ceramics structure homogeneity is one of the most important tasks in the process of high-quality varistor development.

It should be pointed out that the obtained values of grain specific resistance correlates with the data as for their average size: the larger values of grain specific resistance correspond the less values of average size (*tab. 2*). It proves the influence of grain cross section on their specific resistance.

The obtained values of SnO₂ grain specific resistance are several times as large as those of ZnO grains (0.25-0.7 Ohm·cm) in ZnO based varistors [12, 13]. It limits the usage of SnO₂ based ceramics as a varistor material. But the obtained value of 1.1 Ohm·cm for SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO system almost coincides with the value 1.2 Ohm·cm which was found out earlier for

the SnO₂-CoO-Nb₂O₅-Cr₂O₃-Y₂O₃ system. The last one is the least for SnO₂ based varistors [17] and it allows to decrease the grain specific resistance in future.

Conclusions

The coordinated changes of a linear shrinkage, a grain average size, a qualifying electric field, an electric conductivity, activation energy of electric conduction, a nonlinear coefficient, a normalized nonlinear coefficient and a dielectric permittivity prove the barrier mechanism of electric conductivity in SnO₂ based ceramics. The CaO addition improves the nonlinearity of voltage current characteristics of SnO₂ based ceramics. The obtained normalized nonlinear coefficient $b_E = 0.02 \text{ cm} \cdot \text{V}^{-1}$ for SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO-CaO system is the largest for the samples of SnO₂ based ceramics. The values of grain average sizes calculated from voltage current characteristics at high currents correlate with the data of electron microscopy. The estimated on the basis of impulse testing value of SnO₂ grain specific resistance 1.1 Ohm·cm is the lowest among those ones for SnO₂ based ceramics. The increase of burning temperature leads to the decrease of grain specific resistance. The SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO-CaO ceramics is a prospective material for a varistor production.

The authors are very grateful to A.B. Glot (Universidad Tecnológica de la Mixteca) and R. Bulpett (Experimental Techniques Centre, Brunel University) for organizing the scanning electron microscopy.

Гапонов О.В. - к.ф.-м.н., доцент кафедри радіоелектроніки;
Воробйов О.В. - магістр факультету фізики, електроніки та комп'ютерних систем;
Васильєв А.М. - магістр факультету фізики, електроніки та комп'ютерних систем.

[1] T.K. Gupta, J. Am. Ceram. Soc. 73, 1817 (1990).

[2] D.R. Clarke, J. Am. Ceram. Soc. 82, 485 (1999).

- [3] A.B. Glot, A.P. Zlobin, Inorg. Mater. 25 (2), 274 (1989).
- [4] S.A. Pianaro, P.R. Bueno, E. Longo, J.A. Varela, J. Mater. Sci. Lett. 14, 692 (1995).
- [5] P.N. Santosh, H.S. Potdar, S.K. Date, J. Mater. Res. 12, 326 (1997).
- [6] W.-X. Wang, J.-F. Wang, H.-C. Chen, W.-B. Su, G.-Z. Zang, Mater. Sci. Eng. B 99, 457 (2003).
- [7] A.B. Glot, I.A. Skuratovsky, Mater. Chem. Phys. 99 (2 – 3), 487 (2006).
- [8] P.R. Bueno, J.A. Varela, E. Longo, J. Eur. Ceram. Soc. 28 (3), 505 (2008).
- [9] A.B. Glot, A.V. Gaponov, A.P. Sandoval-Garcia, Phys. B: Condensed Matter. 405, 705 (2010).
- [10] A.V. Gaponov, A.B. Glot, Semiconductor Physics, Quantum Electronics & Optoelectronics 14 (1), 71 (2011).
- [11] A.I. Ivon, A.B. Glot, I.M. Chernenko, Fourth Euro-Ceramics. V. 5, Electroceramics (Gruppo Editoriale Faenza Editrice, Faenza, 1995), p. 475.
- [12] A.I. Ivon, A.B. Glot, A.V. Gaponov, S.V. Mazurik, Key Engineering Materials 132-136, 1289 (1997).
- [13] A.I. Ivon, Inorg. Mater. 36 (10), 1074 (2000).
- [14] M.A. Ramirez, W. Bassi, R. Parra, P.R. Bueno, E. Longo, J.A. Varela, J. Am. Ceram. Soc. 91 (7), 2402 (2008).
- [15] M.A. Ramirez, W. Bassi, P.R. Bueno, E. Longo, J.A. Varela, J. Phys. D: Appl. Phys. 41, 122002 (2008).
- [16] Z.-Y. Lu, Z. Chen, J.-Q. Wu, J. Ceram. Soc. Japan 117 (7), 851 (2009).
- [17] A.B. Glot, Z.Y. Lu, Z.Y. Zhou, A.I. Ivon, Superficies y Vacio 24(2), 61 (2011).
- [18] A.V. Gaponov, A.B. Glot, A.I. Ivon, R. Bulpett, Phys. Chem. Solid State 11 (3), 738 (2010), in Ukrainian.
- [19] J.A. Varela, J.A. Cerri, E.R. Leite, E. Longo, M. Shamsuzzoha, R.C. Bradt, Ceram. Int. 25, 253 (1999).
- [20] M.S. Castro, C.M. Aldao, J. Eur. Ceram. Soc. 18, 2233 (1998).
- [21] S.A. Pianaro, P.R. Bueno, P. Olivi, E. Longo, J.A. Varela, J. Mater. Sci.: Mater. Electron. 9, 159 (1998).
- [22] C. Wang, J. Wang, H. Chen, W. Su, G. Zang, P. Qi, M. Zhao, Mater. Sci. Eng. B, 116, 54 (2005).
- [23] A.B. Glot, A.P. Sandoval-Garcia, A.V. Gaponov, R. Bulpett, B.J. Jones, G. Jimenez-Santana, Adv. in Tech. of Mat. and Mat. Proc. J. 10 (1), 21 (2008).
- [24] A.V. Gaponov, A.B. Glot, Vestnik Dnepropetrovsk University 16 (2), 119 (2008), in Russian.
- [25] A.V. Gaponov, A.B. Glot, A.V. Kovalenko, Phys. Chem. Solid State 10 (4), 939 (2009), in Ukrainian.
- [26] A.B. Glot, A.N. Bondarchuk, A.I. Ivon, L. Fuentes, J.A. Aguilar-Martinez, M.I. Pech-Canul, N. Pineda-Aguilar, XIX International Conference on Extractive Metallurgy (Saltillo, Mexico, 2010). P. 572.
- [27] M. Batzill, U. Diebold, Prog. Surf. Sci. 79, 47 (2005).

О.В. Гапонов, О.В. Воробйов, А.М. Васильєв

Електричні параметри варисторної кераміки на основі SnO₂ з домішками оксидів CaO і BaO

Дніпропетровський національний університет ім. Олеся Гончара, пр. Гагаріна, 72, Дніпропетровськ, 49010,
Україна, e-mail: alexei_gaponov@ukr.net

В дослідженій варисторній кераміці SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO додавання оксидів CaO або BaO призводить до зменшення електропровідності в слабкому електричному полі й корельованого збільшення висоти потенціальних бар'єрів на межах зерен SnO₂ (з 0,7 до 1,0 еВ). Координовані зміни електричних параметрів при підвищенні температури випалу з 1520 до 1620 К (збільшення значень лінійної усадки, розміру зерен, електричної провідності, коефіцієнта нелінійності b , нормалізованого коефіцієнта нелінійності b_E і діелектричної проникності та зменшення значень класифікаційної напруженості електричного поля, енергії активації електропровідності й питомого опору зерен) підтверджують бар'єрний механізм електропровідності в кераміці на основі SnO₂. Найбільші значення $b = 58$ і $b_E = 0,02 \text{ см} \cdot \text{В}^{-1}$ має кераміка з домішкою CaO, спечена при 1620 К. За даними імпульсних досліджень в області сильних електричних струмів підвищення температури випалу обумовлює збільшення середнього розміру зерен SnO₂ і зменшення їх питомого опору r_g . Отримане значення $r_g = 1,1 \text{ Ом} \cdot \text{см}$ для кераміки SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃-CuO є найменшим серед визначених в оксидно-олов'яній кераміці. Додавання оксидів CaO або BaO збільшує питомий опір зерен і зменшує їх середній розмір.

Ключові слова: варистор, SnO₂, кераміка, межа зерен, CaO, BaO, електропровідність, питомий опір, розмір зерен.