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ELECTRICAL PROPERTIES OF TIN OXIDE BASED VARISTORS WITH PbO ADDITION IN HUMID AIR

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In order to decrease the humidity sensitivity of SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3 varistor ceramics, lead oxide was added and the electric characteristics of synthesized materials with the PbO concentration of 0, 0.1, 0.5, 0.7, 1 and 2 mol.% in the air with relative humidity of 10–86% were investigated. All tested samples have non-linear current–voltage characteristics with large values of the nonlinearity coefficient of 38–51. The optimal concentration of PbO addition in ceramics is 0.5–0.7 mol.%. The addition of such quantity of lead oxide to the ceramics leads to the decrease of the breakdown electric field up to 4390 V/cm and the humidity sensitivity coefficient up to 172. The increase of the PbO concentration provides the increase of the electrical conductivity of samples at low fields. The barrier mechanism of electrical conductivity of the studied ceramics is proved by the obtained values of potential barrier heights of 0.85–0.90 eV on the SnO_2 crystallite boundaries.

Keywords: varistor, ceramics, SnO_2, PbO, relative humidity

PACS: 73.30.+y, 73.40.Ty, 73.50.Fq

1. Introduction

Tin oxide SnO_2 is widely used for the production of optically transparent conducting materials, gas sensitive sensors and varistors [1–3]. One of the important properties of SnO_2 based semiconductor materials is their great sensitivity to the relative air humidity [3–10]. The electric conductivity of tin oxide ceramics in the low electric field grows with the increase of air humidity [3–9]. The growth of electrical conductivity is undesirable when tin oxide based varistors are produced, especially when they are designed for electronic device overvoltage protection. So, such effect should be avoided or minimized. For this purpose, the surface of ceramic samples is protected with different moisture-resistant films [4, 6] or different additions, mainly those which decrease the moisture influence on SnO_2 crystallite boundaries [3, 5, 7–9].

SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3 ceramics is one of the most investigated systems for varistor production [11–13]. It has great non-ohmic current–voltage characteristics (CVC) with quite a large nonlinearity coefficient $\alpha \approx 40–50$ and at the same time great gas sensitive properties. Nowadays, the actual task is to decrease the sensitivity of this system to the air humidity. Earlier, this effect was achieved with adding Bi_2O_3, V_2O_2 and CuO to the SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3 system [3, 5, 7–9]. Bi_2O_3, V_2O_2 and CuO oxides have low melting temperatures, which are less than burning temperatures of ceramics. The samples with such additions have liquid phases in the process of sintering, that is why the sensitivity of these ceramics to the environment decreases. But the humidity sensitivity coefficient of these samples remains quite large [3].

In order to solve the problem of varistor humidity sensitivity, we decided to add lead oxide to the SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3 system. PbO has the melting point $T_m \approx 886$°C, therefore the synthesis of such ceramics is the liquid-phase one. There are no published papers about the lead oxide addition to such system. The aim of this paper is to study the electrical properties of the obtained ceramic varistors with PbO addition in the environments with different air relative humidity.

2. Experiment

The studied ceramics (99.4–x) SnO_2–0.5Co_3O_4–0.05Nb_2O_5–0.05Cr_2O_3–xPbO (mol.%) with the PbO concentration of x = 0, 0.1, 0.5, 0.7, 1 and 2 mol.% was produced by the traditional ceramic technology. The details of the preparation are described in Ref. [13]. The sample baking was taking place at 1250°C during 1 h. In the process of electrode production, the In-Ga eutectic was applied.

The CVC of the samples were measured in the contained chambers with relative humidity of 10–86% above the surface of the water solution of a proper salt (the details are given in Ref. [8]). The values of nonlinearity coefficient $\alpha = (E/j)\,(\mathrm{d}j/\mathrm{d}E)$ were measured at the current density of j = 1 mA/cm^2. The breakdown electric field E_1 was estimated at the same value of j. The electrical conductivity $\sigma = j/E$ was obtained in the area of low currents. The humidity sensitivity coefficient S was calculated for the $j(E)$ characteristic at the low field by $S = (\sigma_{w2} - \sigma_{w1})/\sigma_{w1}$, where σ_{w1} and σ_{w2} are the electrical conductivity of the sample in the area of low currents at the air relative humidity w_1 = 10% and w_2 = 86%, respectively.

The value of the activation energy of electrical conduction E_σ was calculated with the help of temperature dependences of electrical conductivity in the low electric field by $\sigma = \sigma_0 \exp(-E_\sigma/kT)$, where σ_0 = const, k is the Boltzmann constant, and T is the absolute temperature.

3. Results and discussion

3.1. Electrical characteristics

All obtained $j(E)$ dependences of the samples are greatly non-linear. For small values of the electric field ohmic and low non-linear parts are common while for the strong electric field high non-linear ones are more natural. For example, such situation at the air relative humidity 75% is presented in Fig. 1. Adding of lead oxide to the ceramics slightly decreases the nonlinearity of CVC in the high field as well as the values of nonlinearity coefficient α (Table 1). It is explained by the existing Schottky-type double potential barriers on the SnO_2 crystallite boundaries and the influence of intercrystalline phase. The decrease of grain boundary barrier height and the transference

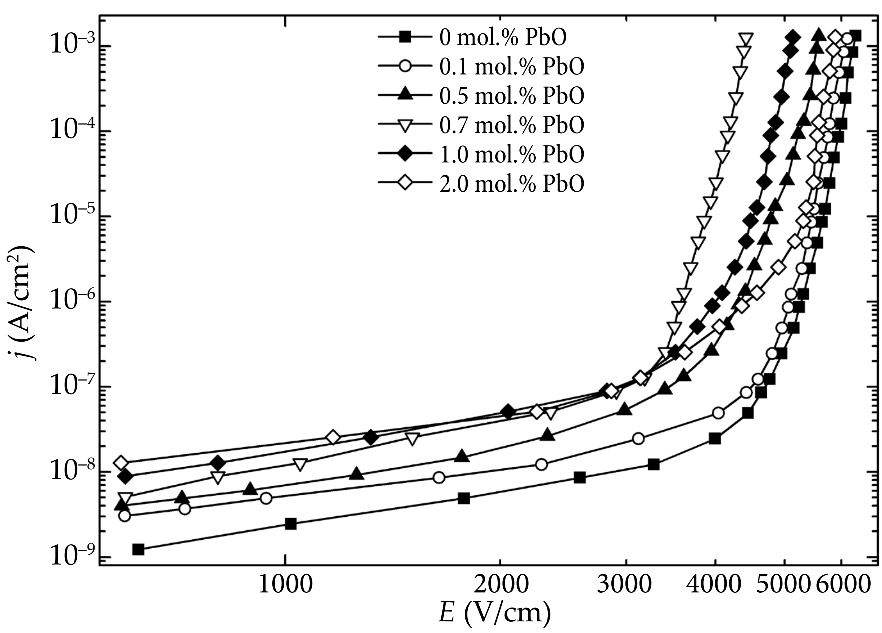

Fig. 1. Current density j vs electric field E in SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3–PbO varistor ceramics with different concentrations of PbO additions in the air with relative humidity 75%.

from high voltage to low voltage varistors are usually accompanied by the decreasing of the nonlinearity of CVC [14–16]. Just the same situation takes place in our experiments, see the detailed discussion below.

Table 1. Electrical parameters of SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3–PbO varistor ceramics with different concentration of PbO additions in the air with relative humidity 75%.

PbO, mol.%	α	E_1, V·cm^{-1}	σ, Ohm^{-1}·cm^{-1}	E_σ, eV	S
0	51.4	6240	$2.0\cdot10^{-12}$	0.90	824
0.1	42.9	6080	$5.1\cdot10^{-12}$	0.90	413
0.5	40.6	5550	$6.8\cdot10^{-12}$	0.85	172
0.7	44.8	4390	$8.5\cdot10^{-12}$	0.86	479
1	37.8	5110	$1.5\cdot10^{-11}$	0.85	953
2	43.9	5860	$2.2\cdot10^{-11}$	0.86	1836

While increasing the concentration of PbO in the samples up to 0.7 mol.%, the high nonlinear part of $j(E)$ characteristic shifts towards the low electric field (Fig. 1) and the values of breakdown electric field E_1 decrease from 6240 to 4390 V/cm (Table 1). The lowest value E_1 = 4390 V/cm is obtained while adding 0.7 mol.% PbO to the ceramics. It is obvious that the small concentration of PbO addition helps to merge SnO_2 grains when baking and fosters their growth by making the best conditions, that is, the fluid phase during baking. Therefore the value of E_1 of the tested varistors decreases when the concentration of PbO increases up to 0.7 mol.%. The further increasing of the lead oxide concentration in ceramics leads to the reverse shift of $j(E)$ characteristic towards the high electric fields (Fig. 1) and the increasing of E_1 (Table 1). It is possible that the forming of a thick lead-containing film between crystallites prevents from their merging at high temperatures. Therefore, the ceramic grains remain quite small and the values of E_1 are bigger. The detailed study of this effect requires additional investigations.

The low voltage varistors have small values of nonlinearity coefficient and quite large conductivity in the low electric field for the oxide-based semiconductor ceramics [3, 17, 18]. It is obvious that such situation also takes place for the tested tin oxide ceramics with PbO addition.

In order to check this hypothesis, we have measured temperature dependences of the electric conductivity of all samples (Fig. 2). The values of activation energy of electrical conductivity E_σ that were calculated from the line slopes in the high temperature part of characteristics are close to the values of the height of potential barriers on the grain boundaries φ_0 [19]. When temperature increases, the electrical conductivity in the low

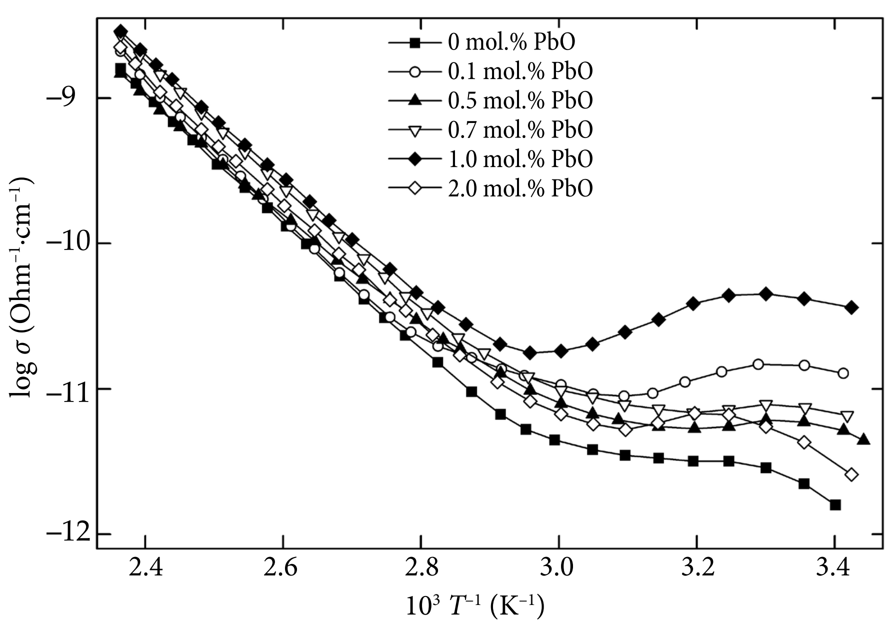

Fig. 2. Temperature dependences of the electrical conductivity of SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3–PbO ceramics with different concentrations of PbO additions.

temperature part decreases. It is connected with the desorption of water molecules from ceramic pores [3, 5, 7–9].

The height of potential barriers of all tested samples is quite high: E_σ = 0.85–0.9 eV. There is a correlation between the values of activation energy E_σ and nonlinearity coefficient α (Table 1). The decrease of the height of grain boundary potential barriers leads to the decrease of the nonlinearity of CVC. On the whole, when adding PbO to the ceramics, the values of E_σ decrease, and this leads to the increase of the electrical conductivity of samples in the low field (Table 1). Thus, in SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3–PbO ceramics the electrical conductivity is mostly controlled by Schottky potential barriers on the SnO_2 crystallite boundaries.

The increase of PbO concentration in the samples leads to the increase of conductivity σ in the low field (Table 1). But the electric conductivity in the low electric field is controlled not only by the potential barriers on SnO_2 grain boundaries but also by intergranular phase resistance. Intercrystalline lead-containing layers that are formed during baking [20] are partially shunting the SnO_2 crystallites. Therefore, the values of the low-field electrical conductivity of samples increase with the increasing of the concentration of PbO addition in ceramics.

3.2. Effect of humidity on electrical characteristics

Electrical characteristics of semiconductor ceramics are mostly dependent on the environment and, first of all, on the humidity of air. In order to check the influence of humidity on the characteristics and parameters of tested materials, the CVC of all samples in the air with relative humidity of 10–86% were registered. For example, the $j(E)$ dependences for the samples with a concentration of PbO 0.5 mol.% are shown in Fig. 3. With increasing the air relative humidity, the low-field part of $j(E)$ characteristic greatly shifts to the larger values of current density, but the high-field part of this characteristic remains almost the same. When decreasing the air relative humidity down to 10%, the values of sample conductivity at the low electric field also decrease. The second experiment proves that this effect is renewed.

The electrical characteristics of tested polycrystalline samples are controlled by the potential barriers on the crystallite boundaries [14–16]. The height of these barriers decreases with increasing the air humidity and the voltage applied to the sample [7, 16]. Therefore, while the air relative humidity increases, the low-field electrical conductivity also increases, especially when the value w changes from 75 to 86% (Fig. 3). The large value of humidity (w = 86%) leads to the great influence of

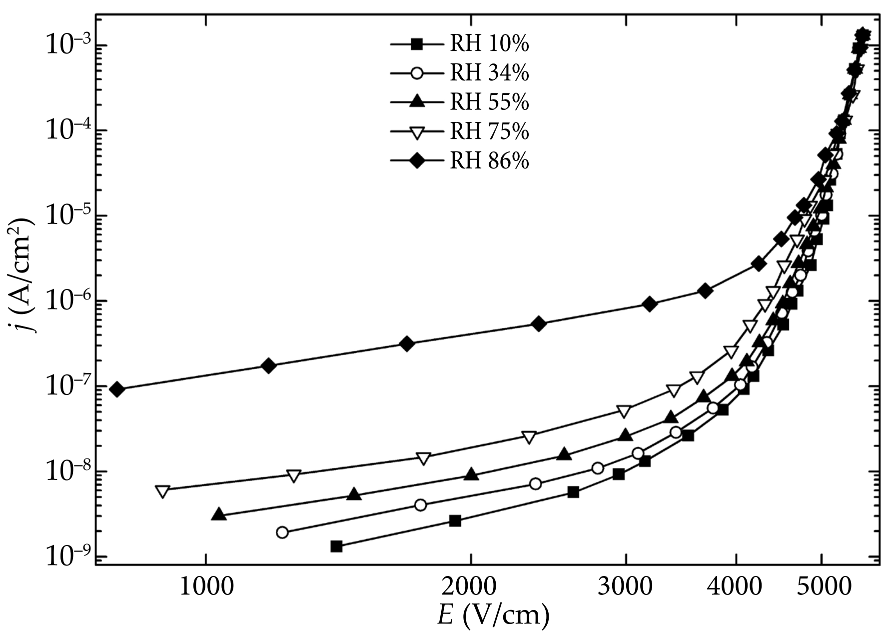

Fig. 3. Current density j vs electric field E_1 in SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3–0.5 mol.% PbO ceramics in the air with different relative humidity.

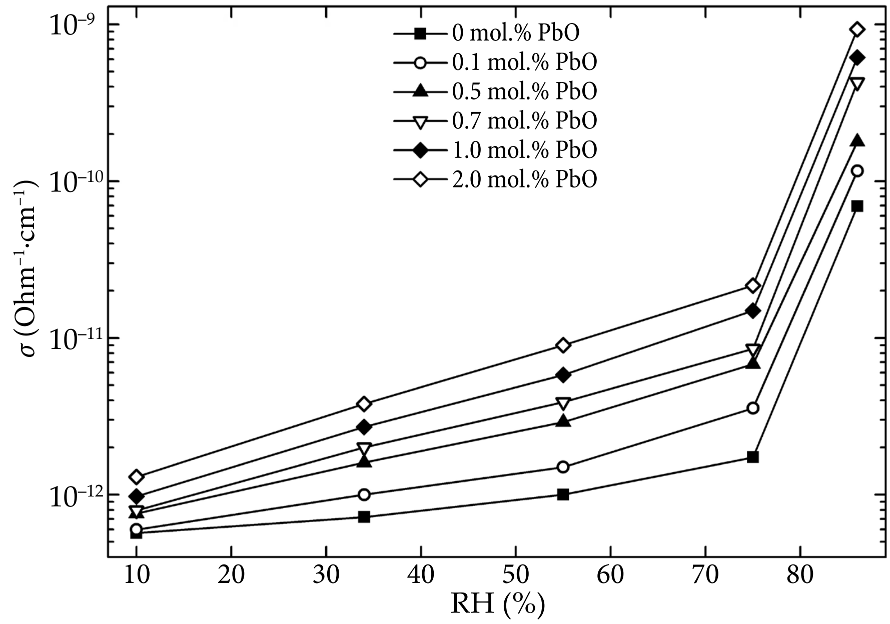

Fig. 4. Low-field electrical conductivity vs relative humidity in SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3–PbO ceramics with different concentrations of PbO additions.

water molecules on the ceramics characteristics. The water molecules penetrate into the ceramic pores and the electrical conductivity of materials increases quite significantly [3, 5]. It is proved by the data of electrical conductivity at the low electric field of all samples with the concentration of PbO 0–2 mol.% in the air with relative humidity of 10–86% (Fig. 4). The electrical conductivity σ at the relative humidity 86% of all samples increases dramatically in comparison with the values σ at $w = 75\%$.

When increasing the air relative humidity, the height of intercrystalline potential barriers decreases but still remains quite large for the varistor effect at the high electric field [7]. With increasing the voltage, the height of these barriers continues decreasing down to the critical value when the current through the sample begins to increase quite dramatically. Therefore, the tested ceramics has high non-linear CVC with the nonlinearity coefficient $\alpha \approx 38$–45 even with the air relative humidity of 75 and 86%.

The value of humidity sensitivity coefficient $S = 824$ of the obtained materials without PbO addition is quite large because of the pores in well-synthesized ceramic samples [9]. The addition of lead oxide up to 0.5 mol.% to the ceramics leads to the decrease of S value to 172 (Table 1). It is caused by the formation of glass-like lead-containing layers between the grains limiting the movable protons H^+, which are formed during the dissociation of the H_2O molecule adsorbed on the surface of sample [3, 5]. Such protons lead to the decrease of intercrystalline potential barrier height and the increase of the electrical conductivity of samples in the low electric field. With increasing of the PbO concentration from 0.7 to 2 mol.%, such protons may penetrate along the formed continuous lead-containing film to the SnO_2 crystallite boundaries and increase the electrical conductivity of ceramics. Therefore the humidity sensitivity of samples with 0.7–2 mol.% PbO additions is quite high (Table 1).

With adding PbO in small quantities into SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3 ceramics, both the humidity sensitivity coefficient S and the breakdown electric field E_1 decrease (Fig. 5). The optimal values of the PbO concentration in ceramics are 0.5–0.7 mol.%. The formation of a more solid and less porous structure because of a small quantity of the lead-containing intergranular phase, which is in a liquid state during synthesis, leads to the decrease of humidity sensitivity of the tested samples. At the same time, the intergranular phase, which was liquid during baking, improves the movement, combining the growth of SnO_2 crystallites,

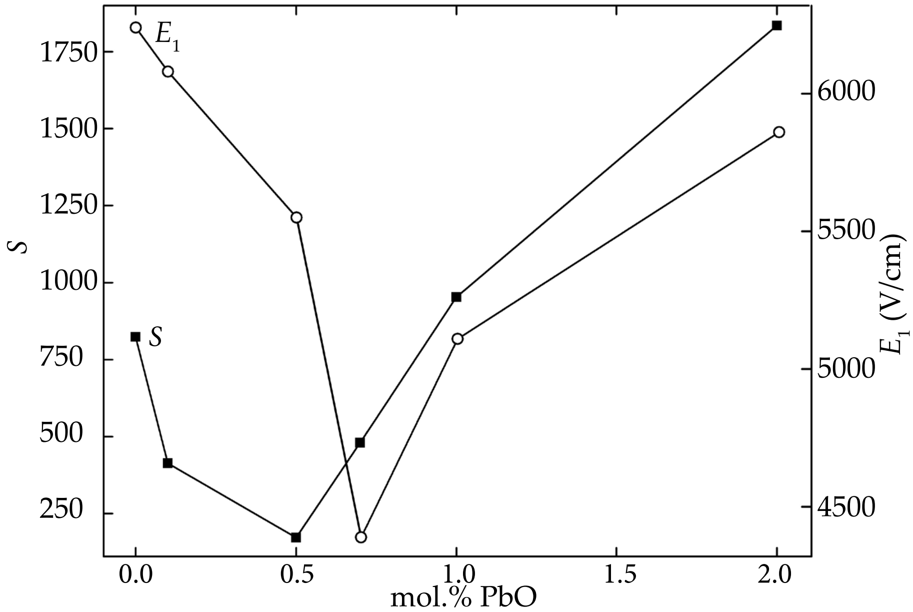

Fig. 5. Humidity sensitivity coefficient S and breakdown electric field E_1 vs the concentration of PbO addition in SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3–PbO ceramics.

and leads to the decrease of breakdown voltage of the obtained varistors.

4. Conclusions

In order to lower the breakdown electric field and simultaneously decrease the humidity sensitivity coefficient of tin oxide ceramics, one can use a small quantity of lead oxide addition. The lowest values of these parameters (E_1 = 4390 V/cm and S = 172) were obtained at the concentration of PbO 0.5–0.7 mol.% in SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3–PbO ceramics. The values of the nonlinearity coefficient of such samples are 41–45. The enhancement of PbO concentration increases the low-field electrical conductivity while passing from high voltage varistors to low voltage ones. The obtained new results help to produce SnO_2 based varistors that are designed for lower voltage and are less sensitive to the environment influence.

References

[1] D.V. Adamchuk, V.K. Ksenevich, N.A. Poklonski, M. Navickas, and J. Banys, Nonstoichiometric tin oxide films: study by X-ray diffraction, Raman scattering and electron paramagnetic resonance, Lith. J. Phys. **59**(4), 224–232 (2019), https://doi.org/10.3952/physics.v59i4.4138

[2] S.M. Ingole, Y.H. Navale, A.S. Salunkh, M.A. Chougule, G.D. Khuspe, and V.B. Patil, Tin oxide nanostructure fabricated by thermal evaporation as potential NO_2 sensor, J. Nano-Electron. Phys. **12**(2), 02024-1–3 (2020), https://doi.org/10.21272/jnep.12(2).02024

[3] A.V. Gaponov and I.A. Skuratovsky, Electrical properties of SnO_2-based varistor ceramics with solid-phase and liquid-phase sintering, J. Phys. Stud. **23**(3), 3708-1–8 (2019), https://doi.org/10.30970/jps.23.3708

[4] E. Traversa, Ceramic sensors for humidity detection: the state-of-the-art and future developments, Sens. Actuat. B **23**(2–3), 135–156 (1995), https://doi.org/10.1016/0925-4005(94)01268-M

[5] I. Skuratovsky, A. Glot, E. Di Bartolomeo, E. Traversa, and R. Polini, The effect of humidity on the voltage-current characteristic of SnO_2 based ceramic varistor, J. Eur. Ceram. Soc. **24**(9), 2597–2604 (2004), https://doi.org/10.1016/j.jeurceramsoc.2003.09.008

[6] Z. Chen and C. Lu, Humidity sensors: a review of materials and mechanisms, Sens. Lett. **3**(4), 274–295 (2005), https://doi.org/10.1166/sl.2005.045

[7] I. Skuratovsky, A. Glot, and E. Traversa, Modelling of the humidity effect on the barrier height in SnO_2 varistors, Mater. Sci. Eng. B **128**(1–3),

130–137 (2006), https://doi.org/10.1016/j.mseb.2005.11.039

[8] A.V. Gaponov, A.B. Glot, A.I. Ivon, A.M. Chack, and G. Jimenez-Santana, Varistor and humidity-sensitive properties of SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3 ceramics with V_2O_5 addition, Mater. Sci. Eng. B **145**(1–3), 76–84 (2007), https://doi.org/10.1016/j.mseb.2007.10.003

[9] A.V. Gaponov, Humidity sensors based on SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3 semiconductor varistor ceramics, Sens. Electron. Microsyst. Technol. **15**(3), 19–30 (2018), https://doi.org/10.18524/1815-7459.2018.3.142041

[10] M. Velumani, S.R. Meher, and Z.C. Alex, Impedometric humidity sensing characteristics of SnO_2 thin films and SnO_2–ZnO composite thin films grown by magnetron sputtering, J. Mater. Sci. Mater. Electron. **29**, 3999–4010 (2018), https://doi.org/10.1007/s10854-017-8342-z

[11] S.A. Pianaro, P.R. Bueno, E. Longo, and J.A. Varela, A new SnO_2-based varistor system, J. Mater. Sci. Lett. **14**(10), 692–694 (1995), https://doi.org/10.1007/BF00253373

[12] W.-X. Wang, J.-F. Wang, H.-C. Chen, W.-B. Su, and G.-Z. Zang, Effects of Cr_2O_3 on the properties of (Co, Nb)-doped SnO_2 varistors, Mater. Sci. Eng. B **99**(1–3), 470–474 (2003), https://doi.org/10.1016/S0921-5107(02)00477-4

[13] A.V. Gaponov, Influence of yttrium oxide addition on the characteristics of SnO_2 based ceramics, Phys. B Condens. Matter **639**, 414010-1–8 (2022), https://doi.org/10.1016/j.physb.2022.414010

[14] A.B. Glot, The conduction of SnO_2 based ceramics, Inorg. Mater. **20**(10), 1522–1523 (1984).

[15] A.B. Glot and A.P. Zlobin, The non-ohmic conduction of tin dioxide based ceramics, Inorg. Mater. **25**(2), 274–276 (1989).

[16] A.B. Glot, A.V. Gaponov, and A.P. Sandoval-Garcia, Electrical conduction in SnO_2 varistors, Phys. B Condens. Matter **405**, 705–711 (2010), https://doi.org/10.1016/j.physb.2009.09.091

[17] V.O. Makarov and M. Trontelj, Sintering and electrical conductivity of doped WO_3, J. Eur. Ceram. Soc. **16**(7), 791–794 (1996), https://doi.org/10.1016/0955-2219(95)00204-9

[18] C.-W. Nahm and C.-H. Park, Microstructure, electrical properties, and degradation behavior of praseodymium oxides-based zinc oxide varistors doped with Y_2O_3, J. Mater. Sci. **35**, 3037–3042 (2000), https://doi.org/10.1023/A:1004749214640

[19] M. Batzill and U. Diebold, The surface and materials science of tin oxide, Prog. Surf. Sci. **79**, 47–154 (2005), https://doi.org/10.1016/j.progsurf.2005.09.002

[20] J.A. Cerri, I.M.G. Santos, E. Longo, E.R. Leite, R.M. Lebullenger, A.C. Hernandes, and J.A. Varela, Characteristics of PbO–$BiO_{1.5}$–$GaO_{1.5}$ glasses melted in SnO_2 crucibles, J. Am. Ceram. Soc. **81**(3), 705–708 (1998), https://doi.org/10.1111/j.1151-2916.1998.tb02393.x

ALAVO OKSIDO VARISTORIŲ SU PbO PRIEMAIŠA ELEKTRINĖS SAVYBĖS DRĖGNAME ORE

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