# The effect of humidity on the voltage–current characteristic of SnO$_2$ based ceramic varistor

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## Abstract

Tin dioxide based ceramics in the SnO$_2$–Bi$_2$O$_3$–Co$_3$O$_4$–Nb$_2$O$_5$–Cr$_2$O$_3$ system exhibit highly non-linear voltage–current characteristics (non-linearity coefficient reaches 55–60 in electric fields of about 3500 V cm$^{-1}$) in parallel with high humidity sensitivity in low electric fields (humidity sensitivity coefficient reaches 10$^5$). Such ceramics can be used for the fabrication of a device with combined varistor and humidity sensor properties. Voltage–current characteristics of ceramics with different amounts of bismuth oxide are studied in air with different relative humidity contents.
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## 1. Introduction

Relative humidity (RH) sensors are widely used in modern electronics for industry and domestic applications, and oxide ceramics are used for the fabrication of robust sensors for use at high RH values.[1,2] On the other hand, many oxide ceramic materials have non-linear dependence of current on voltage due to the existence of grain boundary potential barriers.[3–6]

It has been previously reported that tin dioxide-based ceramics with such additives as zinc oxide, cobaltous oxide and one oxide from the group Bi$_2$O$_3$, SiO$_2$, GeO$_2$ exhibits both non-linear electrical and humidity sensing properties.[5] Such ceramics have non-linear voltage–current characteristics (VCC) in the air with fixed relative humidity value $w$ and an increase of $w$ leads to the shift of VCC to higher current region.[5] It was found as well that the use of bismuth oxide as additive gives a higher non-linearity coefficient $\beta$ but a lower humidity sensitivity coefficient $S$ and the replacement of Bi$_2$O$_3$ for SiO$_2$ or GeO$_2$ causes a decrease of $\beta$ and an increase of

$S$ value.[5] None the less the absolute value of $\beta$ for SnO$_2$–ZnO–Co$_3$O$_4$–Bi$_2$O$_3$ ceramics was quite low (about 10 at $w = 10\%$).[5] Scanning electron microscopy together with X-ray photoelectron spectroscopy proves that bismuth oxide based phase in tin dioxide based non-Ohmic ceramics exists in the form of a very thin (about 10–30 Å thick) layer covering the tin dioxide grains.[6] This can be the reason why Bi$_2$O$_3$ addition decreases the value of humidity sensitivity.[5] A similar behaviour of bismuth oxide in depressing the relative humidity sensitivity was found independently in other oxide humidity sensing material.[7]

Recently the interest to devices with combined properties like, for example, varistor type gas sensor is growing up.[8] Therefore the study of varistor type humidity sensor similar to mentioned above device,[5] but with a higher non-linearity coefficient, would be quite reasonable.

Earlier the SnO$_2$–Co$_3$O$_4$–BaO–Bi$_2$O$_3$–Nb$_2$O$_5$ system was suggested for the preparation of tin dioxide based ceramics with $\beta = 20$.[9] Last years some compositional improvements were performed and values $\beta = 40$ were reached in a SnO$_2$–CoO–Nb$_2$O$_5$–Cr$_2$O$_3$ system.[10] Considering our experience in the field of varistors and humidity sensors, it is possible to think that varistor ceramics in the SnO$_2$–Co$_3$O$_4$–Nb$_2$O$_5$–Cr$_2$O$_3$ system

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might be humidity sensitive though the authors did not study this effect.[10]

Recently we have developed new compositions of tin dioxide-based ceramics $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ with high non-linearity coefficient $\beta = 50$–$60$. In spite of bismuth oxide is included in the mentioned system and therefore humidity sensitivity could be depressed, it was noticed that some changes of electrical parameters at the variation of relative humidity took place. This effect would be interesting to study in respect of the variation of bismuth oxide content.

With this purpose in this paper a range of ceramics in the $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ system with various amounts of bismuth oxide are sintered and voltage–current characteristics of obtained ceramics are studied in air with different relative humidity values.

## 2. Experimental

Ceramics in the $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ system were prepared by the conventional mixed oxide route. Starting oxides were weighted in a proportion (mol%) $(98.5 - x)$ $SnO_2$–$x$ $Bi_2O_3$–$0.5$ $Co_3O_4$–$0.5$ $Nb_2O_5$–$0.5$ $Cr_2O_3$ . After wet-milling with distilled water and drying, the obtained powder was pressed in tablets 11 mm in diameter and about 1 mm thick under axial pressure 45 MPa. Then pressed tablets were sintered in air by heating at a rate 6.5 °C/min up to temperature 1200 °C, fixing this temperature during 1 h, and subsequent cooling to room temperature with the same rate. After grinding of a sintered sample without using water a suitable silver paste was overlapped at flat surfaces and a sample was heat treated in air by slow heating up to the temperature 800 °C, holding this temperature during 10 min and then slowly cooling.

The values of linear shrinkage $\gamma$ were calculated according to the expression:

$$\gamma = (D_0 - D)D_0^{-1}, \tag{1}$$

where $D_0$ and $D$ are diameters of the sample before and after sintering, respectively.

The images of fractured surfaces of ceramics with different amount of bismuth oxide addition was obtained in secondary electrons using a scanning electron microscope.

Voltage–current characteristics were recorded by applying d.c. voltage and measuring the current. Voltage was increased and decreased with the rate 30 V/min. Possible self heating of a sample during the measurement was detected as an increase in current at a fixed voltage. The results in this paper were obtained avoiding the self heating of samples. Obtained data are presented as dependence of current on voltage. The size of all samples was approximately equal (diameter 10 mm and thickness 1 mm) taking into account humidity

sensing properties and possible inhomogeneous distribution of current over the cross-section of a sample.

Fixed values of relative humidity in air in the 10–85% range were obtained by putting a sample in a closed chamber above the surface of water solution of a proper salt for a time of about 1 h before starting the measurement.

The non-linearity coefficient

$$\beta = \frac{R_s}{R_d} = \frac{U}{I}\frac{dI}{dU}, \tag{2}$$

where $R_s = U/I$ is static and $R_d = dU/dI$ is differential (dynamic) resistance of varistor, $U$—voltage, $I$—current, was estimated as the slope of VCC plotted in double logarithmic coordinates at current density $10^{-3}$ A cm$^{-2}$. Electric field $E_1$ was obtained according to the expression $E_1 = U_1/d$, where $U_1$ is voltage measured at current density $10^{-3}$ A cm$^{-2}$ and $d$ is a thickness of a sample.

The humidity sensitivity coefficient $S$ for the purposes of the present study was defined as the ratio of relative change of current $I(w)$ at fixed low voltage to relative change of relative humidity $w$:

$$S = \frac{I(w_2)/I(w_1)}{w_2/w_1} \tag{3}$$

and was calculated using VCC obtained at different values of relative humidity.

Temperature dependence of electrical conductance was measured in air at low voltage (Ohm's law took place) by heating and cooling of a sample at a rate about 4 °C/min. Electrical conductance was obtained as ratio $G = I/U$. As a result of relative humidity change the outer parts of a ceramic sample might be more conductive. Therefore for the presentation of experimental data electrical conductance $G$ is used instead of electrical conductivity $\sigma = G(d/A)$, where $d$ is thickness of a sample, $A$ is square of a sample cross-section. The values of electrical conductivity $\sigma$ are used for compare the properties of ceramics in air with low relative humidity ($w = 10\%$).

## 3. Results and discussion

Ceramics without bismuth oxide addition contains quite large tin dioxide grains of about 3–7 μm and a lot of very small grains (under or about of 1 μm) of, possibly, another phase (Fig. 1 a). The addition of 0.5 mol% of $Bi_2O_3$ caused the disappearance of the small grained phase, and mostly tin dioxide grains of about 3–7 μm were observed, in a fairly dense sintered ceramics (Fig. 1b). In this case only a very small amount of small grained phase can be seen in pockets between the larger grains. The reason for the disappearance of the small grained phase in the case of bismuth oxide addition can
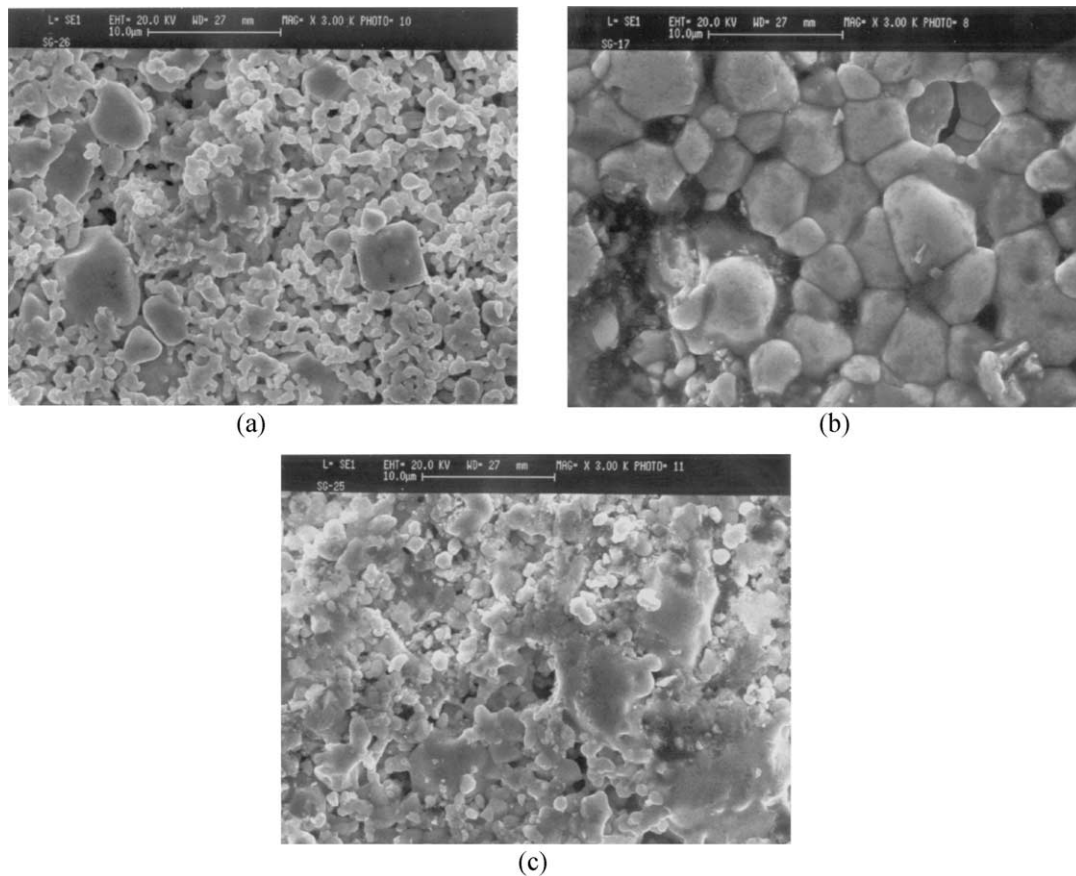
Fig. 1. SEM micrograph of fractured surfaces of ceramics of the $SnO_2$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ system with different amount of bismuth oxide addition: (a) without bismuth oxide; (b) 0.5 mol% $Bi_2O_3$; (c) 1.0 mol% $Bi_2O_3$.

be the liquid phase sintering of ceramics due to the low melting point of $Bi_2O_3$ ($T_m = 820$ °C). The liquid phase sintering is confirmed by the higher linear shrinkage $\gamma$ of sintered samples in the presence of bismuth oxide as it can be concluded from Table 1. The increase of the linear shrinkage means the increase of relative density and decrease of total porosity of obtained material. Meanwhile, the linear shrinkage was measured directly and therefore this parameter will be used further in the discussion.

The presence of the liquid phase promotes as well more homogeneous distribution of additives through the sintered sample and changes chemical reactions during sintering. The addition of 1 mol% of $Bi_2O_3$ gives ceramics with tin dioxide grains covered by quite large amount of melted and solidified bismuth oxide based phase as well as by small grains of that phase (Fig. 1c).

A typical temperature dependence of the electrical conductance $G$ of $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$

Table 1
Some parameters of ceramics in the $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ system with different amount of bismuth oxide

| Concentration of $Bi_2O_3$ (mol%) | 0 | 0.3 | 0.5 | 0.7 | 1.0 |
|---|---|---|---|---|---|
| Linear shrinkage $\gamma$ | 0.064 | 0.14 | 0.17 | 0.16 | 0.14 |
| Electrical conductivity $\sigma$ ($Ohm^{-1}$ $cm^{-1}$) | – | $6 \times 10^{-10}$ | $3 \times 10^{-11}$ | $2 \times 10^{-11}$ | – |
| Activation energy of electrical conduction $E_\sigma$ (eV) | 1.1 | 1.0 | 1.2 | 1.5 | 1.55 |
| Humidity sensitivity coefficient $S$ | 1.5 * | 12.0 | $7.7 \times 10^2$ | $1.2 \times 10^5$ | 80 * |
| Electric field at current density $10^{-3}$ A $cm^{-2}$ $E_1$ (V $cm^{-1}$) | $\sim 2 \times 10^4$ | 4860 | 3500 | 4450 | $\sim 1.5 \times 10^4$ |
| Non-linearity coefficient $\beta$ | $\sim 5$ | 14.6 | 55 | 50 | $\sim 7$ |

Values of humidity sensitivity coefficient $S$ are calculated for current at electric field 1500 V $cm^{-1}$ at relative humidity $w_1 = 10\%$ (or 56% for data marked by the symbol *) and $w_2 = 85\%$. Values of electrical conductivity $\sigma$ are calculated from d.c. current at low voltage (in the region of Ohm's law) at temperature 300 K and relative humidity $w_1 = 10\%$. Values of activation energy of electrical conduction $E_\sigma$ are estimated from $\sigma(T)$ curves at heating of a sample.

ceramics is presented in Fig. 2. It was found that in the range just above room temperature heating causes a decrease in conductance instead of its expected increase (Fig. 2, curve 1). Then at higher temperatures, conductance $G$ is increased with temperature according to the Arrhenius law:

$$G = G_0 \exp\left(-\frac{E_\sigma}{kT}\right), \tag{4}$$

where $G_0$ is a constant, $E_\sigma$ activation energy of electrical conduction process, $k$ Boltzmann constant, $T$ absolute temperature. The estimated value $E_\sigma = 1.2$ eV can be related roughly to the height of grain boundary (GB) potential barrier in the studied ceramics. For simplicity the model of uniform GB potential barriers is assumed to be applicable. The found value is in agreement with the value (1.1 eV) for grain boundary potential barriers in ceramics $SnO_2$–$CoO$–$Nb_2O_5$–$Cr_2O_3$.[11] Considering a more realistic model of ceramics with different heights of GB potential barriers, one can refer $E_\sigma$ as a percolation level.

Cooling the sample from the maximum temperature to room temperature leads to similar dependence though slightly shifted to higher conductance (Fig. 2, curve 2). The mentioned shift of the whole curve can be explained by some desorption of oxygen chemisorbed at grain boundaries. Such process can cause a lowering of GB potential barriers and can slightly decrease the activation energy $E_\sigma$. In accordance to experimental data of Fig. 2 the $E_\sigma$ value is decreased indeed from $E_\sigma = 1.2$ eV for heating to $E_\sigma = 0.9$ eV for cooling. Further cooling to room temperature causes an increase in conductance (Fig. 2, curve 2).

The most strange feature of $G(T)$ dependence shown in Fig. 2 is the anomalous and fairly reproducible low temperature part. The observed decrease in conductance with heating and increase in conductance with cooling
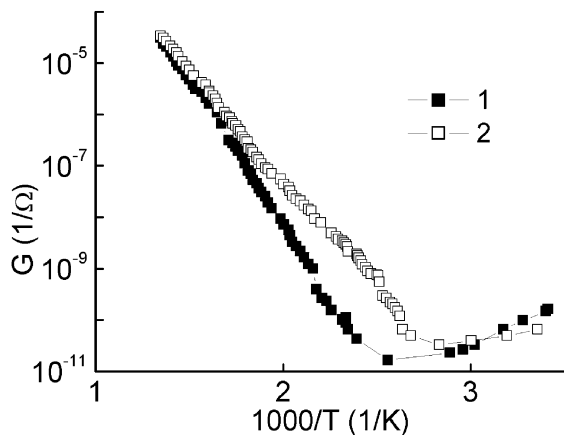


Fig. 2. Temperature dependence of electrical conductance of $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ (0.5 mol% $Bi_2O_3$) ceramics measured in air (1—heating, 2—cooling).

in the range between room temperature ($\approx$20 °C) and below the boiling point of water (100 °C) can be rationalized under assumption of desorption (adsorption) of water from (to) the surface of ceramics with heating (cooling), respectively. The studied ceramics can be humidity sensitive material and some water can exist at the ceramic surface in air at normal conditions. Adsorbed water molecules can dissociate at the surface according to the reaction:

$$H_2O \leftrightarrow H^+ + OH^- \tag{5}$$

and quite mobile proton $H^+$ can penetrate to the region near the grain boundary. Due to the interaction of $H^+$-ion to chemisorbed oxygen in the $O^-$ state, the total negative charge at GB can become lower (on absolute value) leading to the decrease of GB potential barrier height and subsequent increase in conductance. Therefore in air with a given relative humidity, the electrical conductance of studied ceramics is slightly higher than in dry air. As a result of heating the desorption of water from the surface takes place and conductance lowers, but at higher temperatures the process of electrons activation over GB potential barriers become dominant and conductance is raised (Fig. 2). Cooling to room temperature shifts the adsorption–desorption equilibrium to adsorption and conductance grows, which is in accordance to experimental data (Fig. 2).

Barrier mechanism of electrical conduction is supported independently by the observation of the increase in capacitance of tin dioxide-based non-Ohmic ceramics of other compositions at higher relative humidity together with the observed increase in a.c. conductivity.[12] One can assume that similar barrier controlled conduction takes place in other tin dioxide based non-Ohmic ceramics including the discussed one.

Therefore voltage–current characteristics of this ceramics were studied in air with fixed relative humidity. Figs. 3–7 show VCC of ceramics obtained with different amounts of bismuth oxide and measured in air with different relative humidity values. The electrical parameters calculated from these characteristics are reported in Table 1. Let us consider first the VCC of ceramics with the best non-Ohmic properties (with addition of 0.5 mol% $Bi_2O_3$) and ceramics obtained without the addition of bismuth oxide.

At the lowest relative humidity $w = 10\%$, conductance of a sample with addition of 0.5 mol% $Bi_2O_3$ at low electric fields is very low so VCC are shown only at higher fields (higher currents) and the non-linearity coefficient is $\beta = 50$ (Fig. 3, curve 1). At higher relative humidity VCC is non-linear as well. The higher the relative humidity, the higher the conductance at low electric fields (Fig. 3). At relative humidity $w = 34$–85% the part of VCC with low non-linearity coefficient
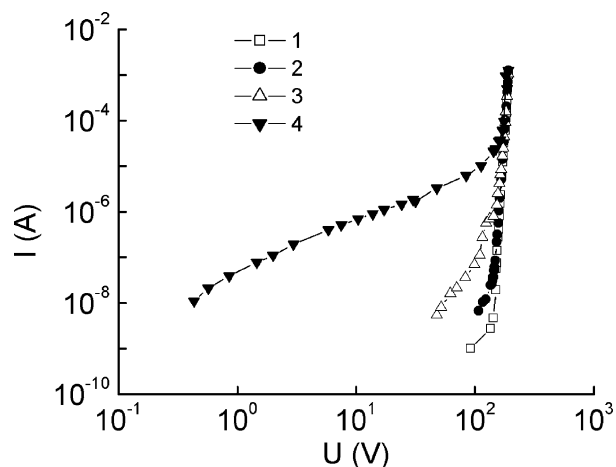
Fig. 3. Voltage–current characteristics of $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ (0.5 mol% $Bi_2O_3$) ceramics in air with different relative humidity values (%): 1 — 10, 2 — 34, 3 — 56, 4 — 85.



Fig. 6. Voltage–current characteristics of $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ (0.7 mol% $Bi_2O_3$) ceramics in air with different relative humidity (%): 1 — 10, 2 — 34, 3 — 56, 4 — 85.



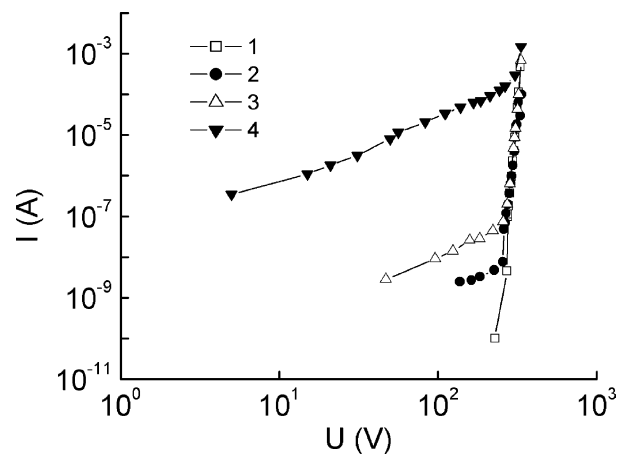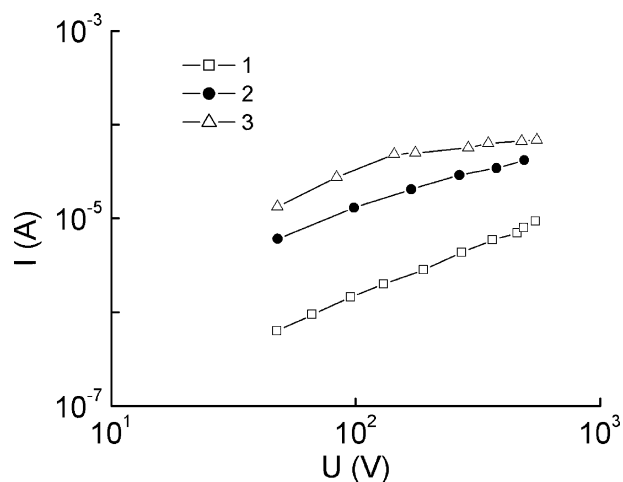Fig. 4. Voltage–current characteristics of $SnO_2$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ ceramics (without of bismuth oxide addition) measured in air with different relative humidity (%): 1 — 34, 2 — 56, 3 — 85.
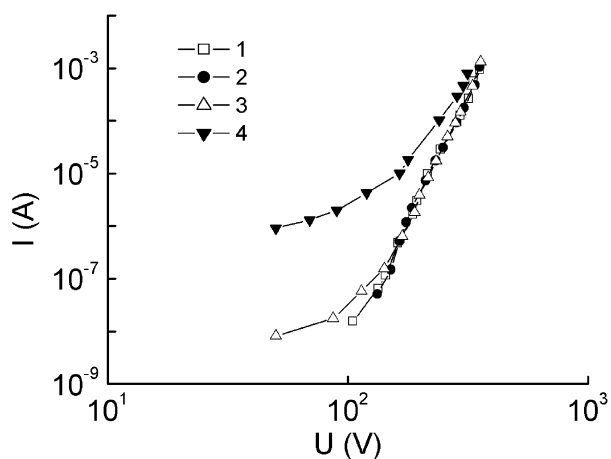


Fig. 7. Voltage–current characteristics of $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ (1 mol% $Bi_2O_3$) ceramics in air with different relative humidity (%): 1 — 56, 2 — 85.

($\beta = 3$–5) is seen at low electric fields and VCC becomes highly non-linear at higher fields (Fig. 3). The highly non-linear part of VCC is not influenced by the variation of relative humidity. On the contrary, low non-linear part of VCC observed at the low electric fields is strongly shifted to higher current region in response to an increase in RH (Fig. 3). This means that highly non-linear VCC of $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ ceramics is due to the intrinsic processes in a solid state phase and atmosphere has a negligible influence on these processes. Ambient air can only affect the conductance at low electric fields.

It can be assumed that highly non-linear $I(U)$ dependence in studied ceramics $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ (as well as in zinc oxide ceramics)[3,4] can be attributed to the tunnelling through GB potential barriers or to the impact ionization in a reverse biased part of GB potential barriers. Such



Fig. 5. Voltage–current characteristics of $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ (0.3 mol% $Bi_2O_3$) ceramics in air with different relative humidity (%): 1 — 10, 2 — 34, 3 — 56, 4 — 85.
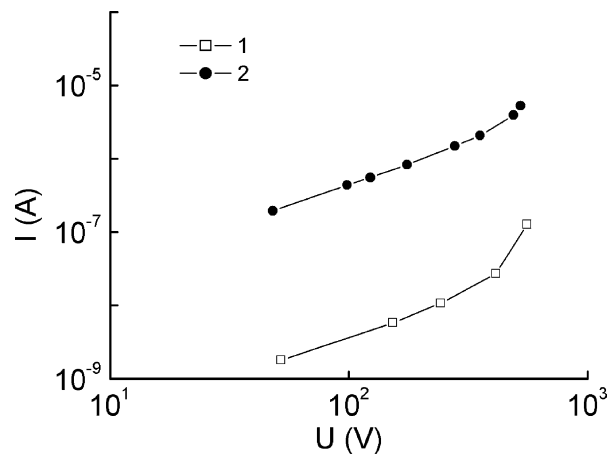
processes are not directly dependent on relative humidity of ambient air.

However, weakly non-linear $I(U)$ dependence at low electric fields is more sensitive to the variation of relative humidity due to the mechanism of electrical conduction at low fields is mainly over-barrier (thermionic emission) and current is strongly dependent on the height of GB potential barriers.

Actually the properties of inner parts of a sample can be weakly dependent on air humidity though the properties of outer parts of a ceramic sample are strongly influenced by humid air due to the penetration of air into the sample through the pores. Penetrated water molecules can promote the decrease in the barrier heights and the last effect can indirectly change the tunnelling or impact ionization current at a fixed voltage.

Therefore, 0.5 mol% of added bismuth oxide ceramics is characterized by the highest non-linearity coefficient in a range of 50–60 (Fig. 3) together with relatively high values of humidity sensitivity coefficient $S = 7.7 \times 10^2$ (Table 1). This is due to the existence of quite high potential barriers at grain boundaries (Table 1). Sufficiently high value of humidity sensitivity coefficient of tin dioxide-based non-Ohmic ceramics with $Bi_2O_3$ addition reflects rather the existence of relatively high GB potential barriers (which can be decreased in humid air atmosphere) than the existence of high total porosity only.

To support this statement it is necessary to note that the addition of $Bi_2O_3$ causes some increase of linear shrinkage up to about 15% . It means that total porosity becomes lower and humidity sensitivity coefficient should become lower as well (if barrier effects are negligible). However, on the contrary, according to the experiment, humidity sensitivity is increased significantly (Table 1). It is due to the barrier nature of humidity sensitivity effect: conductance is dependent on the height of GB potential barriers exponentially [see expression (4)] and therefore some slight decrease of GB barriers height on relative humidity can cause strong increase of conductance. In this case conductance can be changed on the value of RH exponentially.

Considering the situation when conductance of ceramics is controlled by GB potential barriers with the height $\varphi_{GB}(w)$ (in the case of $Bi_2O_3$ addition ) and assuming simple linear relation between $\varphi_{GB}(w)$ and relative humidity $w$:

$$\varphi_{GB}(w) \cong \varphi_{GB0} - \eta w, \tag{6}$$

where $\eta$ is constant coefficient, RH dependence of conductance can be presented as:

$$G(w) \propto \exp\left(-\frac{\varphi_{GB}(w)}{kT}\right) \propto \exp\left(-\frac{\varphi_{GB0}}{kT}\right)\exp\left(\frac{\eta w}{kT}\right). \tag{7}$$

In this case the value of conductance can be very sensitive to RH change.

It was found that ceramics without $Bi_2O_3$ addition have practically linear VCC and an increase in relative humidity shifts the VCC to high current region (Fig. 4). Ceramics without $Bi_2O_3$ is weakly sintered, as it is seen in Fig. 1 and can be concluded as well from the lower value of linear shrinkage in this case in comparison with ceramics with addition of bismuth oxide (Table 1). $SnO_2$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ ceramics have higher conductivity (Fig. 3 and 4) and slightly lower value of activation energy $E_\sigma$ (Table 1) than ceramics with addition of $Bi_2O_3$. Therefore, it is possible to assume that conduction of $SnO_2$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ ceramics is controlled by the necks between grains (by the sizes of the depletion regions of grains in the vicinity of the necks) rather than by potential barriers at grain boundaries. This can be independently supported by the observed fact that $SnO_2$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ ceramics have linear VCC (Fig. 4). This is conformed as well with relatively high value of activation energy of electrical conduction $E_\sigma = 1.1$ eV (Table 1).

Humidity sensitivity coefficient for $SnO_2$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ ceramics ($S = 1.5$) is lower than the value of it for $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ ceramics (Table 1). This can be caused by the different nature of humidity sensitivity effect in ceramics without $Bi_2O_3$. In this case adsorption at $SnO_2$ surface of water molecules penetrated inside the sample can decrease the height of potential barriers at the surface of $SnO_2$ grains and at the surface of necks between $SnO_2$ grains. Therefore the size of the depletion regions in the vicinity of the necks in the direction of electric field is lowered and conductance of ceramics is increased. But in this case the dependence of conductance on the value of RH can be much weaker and humidity sensitivity coefficient for ceramics without $Bi_2O_3$ can be lower than in the case of GB potential barriers controlled conduction (for ceramics with the addition $Bi_2O_3$).

For the illustration of such a situation let us consider the simple model of ceramics with identical necks between neighbouring identical spherical $SnO_2$ grains. It is assumed that due to the adsorption of oxygen the surface potential barriers with the height $\varphi_S$ and the depletion layer thickness $L_S$ exist at the whole surface of $SnO_2$ and $\varphi_S$ (and $L_S$) do not depend on the position at the surface of $SnO_2$. In the Schottky approximation, $\varphi_S \propto L_S^2$. Suppose that two $SnO_2$ grains with grain size $l_g$ are contacted through the neck with diameter $D_N \leqslant 2L_S \ll l_g$. Suppose as well that conductance $G$ of ceramics is controlled by the sizes $L$ of the depletion regions (measured along the electric field) in the vicinity of the necks but charged interfaces between grains and respective potential barriers do not exist, $G \propto L^{-1} \propto L_S^{-1}$. Adsorption of water molecules can reduce the height of surface potential barrier $\varphi_S$ and the

value of depletion layer thickness $L_S$. In the assumption of simple linear relation $\varphi_S = \varphi_S(w) \cong \varphi_{S0} - \eta w$, between $\varphi_S$ and relative humidity $w$, which is similar to the expression (6), conductance of ceramics can be written in a form:

$$G(w) \propto (\varphi_{S0} - \eta w)^{-1/2}. \tag{8}$$

The case $D_N \geqslant 2L_S$ can give some conductive channel between grains with diameter $D = D_N - 2L_S$. Then conductance:

$$G(w) \propto D^2 \propto \left(D_N - 2A(\varphi_{S0} - \eta w)^{1/2}\right)^2, \tag{9}$$

where $A$ is a constant. But the existence of conductive channel between grains is not conformed with the high value of activation energy of electrical conduction $E_\sigma = 1.1$ eV (Table 1). Both expressions (8) and (9) give rising $G(w)$ dependence but fairly weak one.

From the comparison of the Eqs. (7) and (8) it is evident that relative humidity dependence of conductance can be much stronger in the case if conduction is controlled by GB potential barriers [expression (7)], than if conduction is controlled by the necks between grains [expression (8)]. The higher sensitivity of conductance to the variation of relative humidity is observed for those ceramics which contains humidity sensitive potential barriers at grain boundaries.

At low content of $Bi_2O_3$ (0.3 mol%) very weak non-linearity of VCC ($\beta = 14$) is observed (Fig. 5) together with sufficiently low humidity sensitivity coefficient $S = 12$ (Table 1). In this case bismuth oxide, due possibly to its small content, is distributed inhomogeneously and sufficiently high potential barriers are created not at all grain boundaries. As a result, conductance at low voltage and at low relative humidity is quite high and as a consequence the values of $\beta$ and $S$ are low.

The increase of the amount of added $Bi_2O_3$ up to 0.7 mol% gives quite high non-linearity coefficient $\beta = 50$ (Fig. 6). In this case humidity sensitivity at low electric fields is very high ($S = 1.2 \times 10^5$). At more high content of $Bi_2O_3$ addition (1 mol%) conductance of ceramics at low electric fields is low (Fig. 7) though the linear shrinkage is large (Table 1) due to liquid phase sintering in the presence of bismuth oxide. Non-linearity of VCC in this case is poor (Fig. 7). Such behaviour can be explained by the action of two factors: (i) by possible role of bismuth oxide based layers between grains that give additional resistance, or (ii) by the shift of highly non-linear part of VCC to much higher electric fields due to average grain size is decreased and more grain boundaries for unit of length appear. Both options can work together as well.

It is necessary to stress that according to presented data the highest values of humidity sensitivity coefficient $S$ are observed for those ceramics (with addition of 0.5–0.7 mol% of bismuth oxide) which have the highest values of non-linearity coefficient $\beta$ (Table 1). The first impression is like there is a contradiction: higher humidity sensitivity must be observed in the case if surface of $SnO_2$ grains is more accessible for water molecules (small quantity of bismuth oxide addition) though in this case the non-linearity of VCC should be low due to the absence of bismuth oxide at a majority of grain boundaries (bismuth oxide is responsible for the creation of quite high grain boundary potential barriers). But there is no such a contradiction because studied ceramics is obviously grain boundary controlled material and humidity sensitivity of conductance is observed due to the two main factors—the total porosity of ceramics which promotes the penetration of a humid air into the sample and the existence of grain boundary potential barriers. The decrease of potential barriers heights due to the adsorption of water causes the increase of conductance. It means that humidity sensitivity coefficient $S$ should be higher for ceramics with higher potential barriers and the value of the non-linearity coefficient $\beta$ should be higher as well. The nature of the effect of humidity sensitivity of electrical conductance in studied tin dioxide-based ceramics is barrier as well as the mechanism of electrical conduction in this material.

To illustrate additionally this feature of tin dioxide based ceramics it is worth to note, for example, that the difference between the values of current at low electric fields for relative humidity 34 and 85% is about one, two and four orders of magnitude for ceramics with the addition of 0 (Fig. 4), 0.5 (Fig. 3) and 0.7 mol% of bismuth oxide (Fig. 6), respectively.

## 4. Conclusions

Ceramics in the $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ system combine the properties of humidity sensor and varistor. Depending on the concentration of bismuth oxide added the same ceramic sample behaves as humidity sensor with the humidity sensitivity coefficient $S$ up to $1.2 \times 10^5$ at low electric fields and as varistor with the non-linearity coefficient $\beta = 50$–60 at higher electric fields $E_1 = 3500$–4500 V cm$^{-1}$ (at current density $10^{-3}$ A cm$^{-2}$). The grain boundary potential barriers created in ceramics during sintering are responsible for electrical conduction, determining high humidity sensitivity at low electric fields and abrupt non-Ohmic behaviour at high fields.

The conduction of $SnO_2$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ ceramics (without of $Bi_2O_3$) is controlled by the necks between grains rather than by grain boundary potential barriers. The neck controlled conduction of $SnO_2$-based ceramics is less humidity sensitive than grain boundary controlled one.

Ceramics in the $SnO_2$–$Bi_2O_3$–$Co_3O_4$–$Nb_2O_5$–$Cr_2O_3$ system can be used for the fabrication of a device with combined varistor and humidity sensor properties.

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