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Voltage-current characteristics of vanadium dioxide based ceramics

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Abstract

Voltage-current characteristics of VO_2 and V_2O_5–P_2O_5 glasses based ceramics with an addition of copper has been studied. The voltage-current characteristics are of S-type and have behaviour, which is typical for materials on the basis of vanadium dioxide. At some voltage the switching takes place and in a ceramic sample is formed the channel of electrical current. The VO_2 crystallites in this channel are in a metallic phase. The analytical expression for a voltage-current characteristic of a ceramic sample with the cylindrical channel of electrical current is obtained. The effective electrical conductivity and effective thermal conduction of vanadium dioxide based ceramics are increasing, the switching voltage is decreasing at increase of the content of copper additive. The probable reason of that is increase of amount of electrical and thermal bonds between VO_2 crystal grains through inclusions of copper, and also the decrease of a porosity of ceramics.

Keywords: Electrical conductivity; Metallic inclusions; Switching; Voltage-current characteristics; VO_2; V_2O_5–P_2O_5

1. Introduction

Earlier we reported about synthesis of a ceramic material on the basis of vanadium dioxide (VO_2) and V_2O_5–P_2O_5 glasses.[1] As known VO_2 and materials on the basis of VO_2 represent practical interest for the thermistors[2] and threshold switches.[3–5] Such application of these materials is connected with semiconductor-metal phase transition in the vicinity of temperature $T_t = 68$ °C.[5] This phase transition gives the resistivity jump in the vicinity of temperature T_t. The value of this jump equals a few decades. The investigation of crystals and films of VO_2[4–6] showed that they have a voltage-current characteristic (VCC) of S-type with the threshold of switching. The switching has an electrothermal nature and is connected with a heating-up of vanadium dioxide by an electrical current up to temperature T_t.[5]

The voltage-current characteristics of VO_2 based ceramics were not investigated. Such data are interesting for development of the limiters of electrical current. This current limiters can be used for protection of the electric equipment from starting currents.[2]

The aim of this work is the investigation of voltage-current characteristics of vanadium dioxide based ceramics.

2. Experimental

The ceramics of composition (wt.%) xCu-15VPG-(85-x)VO_2 ($x = 1$–5) has been studied in this work. Where VPG is vanadium phosphate glass of composition (mol%) $80V_2O_5$–$20P_2O_5$. The powder of copper was used as additive. The ceramics was obtained by technology described by us earlier.[1] The sintering of ceramics at the temperature (950 ± 10)°C in an atmosphere of helium has been made.

The samples for investigation had diameter of 12 mm and thickness in a range of 1–2 mm for different samples. The electrodes were obtained by a vacuum deposition of indium or by electrodeposition of copper. The results in both cases were identical.

The voltage-current characteristics at environment temperature of (20 ± 0.5) °C has been measured. For

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limitation of an electric current at measurements of VCC, resistor was included sequentially with a sample of ceramics. Electrical resistance of this resistor we chose in an interval 10–40 Ohm. The electrical current through the sample has been determined by measurement of voltage drop on the resistor of (1±0.001) Ohm, which was included sequentially with a sample. A voltage on resistor and a sample of ceramics have been measured by digital voltmeter with a relative error no more than ±0.5%. This voltages have been recorded after reaching a temperature balance between a sample and environment, when the stationary value of the current through a sample has been reached.

3. Results and discussion

The typical voltage-current characteristic of vanadium dioxide based ceramics is shown on Fig. 1. The voltage-current characteristic has threshold behaviour as well as for crystals and films of VO_2.[4–6] The switching of ceramic sample to a low electrical resistance takes place when the electric intensity reaches some threshold value E_S. Dotted lines on Fig. 1 connect points between which a switching takes place. The arrow shows a direction of switching. The slope of a dotted lines depends from an electrical resistance included sequentially with a sample of ceramics. The values of a current in ceramic sample after switching exceed more than at ten times similar values of current for the crystals and films of VO_2[4,5] and also for glasses on basis of vanadium oxides.[8]

Two regions can be determined for the voltage-current characteristic of vanadium dioxide based ceramics. In Fig. 1 the region 1 match a semiconductor phase of

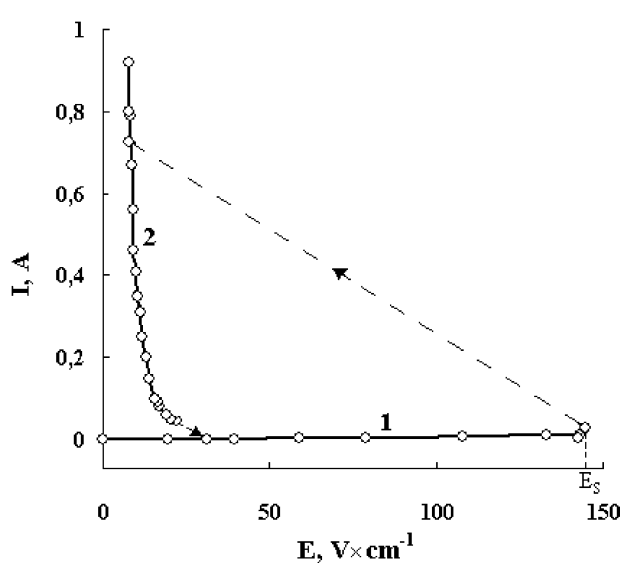


Fig. 1. Voltage-current characteristic of ceramics (wt.%) $84VO_2$–15VPG–1Cu.

VO_2 crystal grains in all volume of a sample. The electrical resistance of a sample for this region is high and the voltage-current characteristic have a shape which is typical for semiconductor thermistors. In Fig. 1 the region 2 has negative differential electrical resistance. Region 2 match the existence of a channel of electrical current in ceramic sample. In this channel the crystal grains of VO_2 are in a metal phase and have high conductivity. The channel of electrical current is forming when the power is sufficient for heating up of ceramic sample to the temperature of a phase transition in vanadium dioxide T_t.

The calculation using the model of "critical temperature" gives the formula for the voltage of switching U_S[5]:

$$U_s = \left[\frac{\alpha(T_t - Q)}{\sigma_t}\right]^{\frac{1}{2}}, \quad (1)$$

where α is the combination of thermal parameters and geometrical sizes of a sample; T_t is the temperature of metal-semiconductor phase transition; Q is the environment temperature; σ_t is the conductivity of VO_2 in semiconductor phase near the temperature T_t.

Formula (1) satisfactorily describes experimental results for the films and crystals of VO_2 at the temperature region $T > 0$ °C.[5] The application of formula (1) for vanadium dioxide based ceramics requires looking through the features of this material.

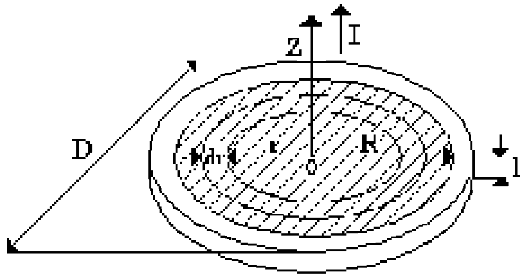
According to the data of scanning electron microscopy, ceramics investigated in this work is a heterogeneous material consisting from chaotically oriented VO_2 crystallites, glass inclusions and pores.[7] It is known that outside the area of a percolation threshold the electrical conductivity of a heterogeneous material can be described by the theory of effective medium.[9] In this theory the homogeneous medium with effective values of parameters is used as replacement of heterogeneous medium.

If the results of theory of effective medium are used for vanadium dioxide based ceramics, then σ_t in formula (1) is an effective electrical conductivity. The formula (1) can be represented for thin ceramic samples as:

$$E_s = \left[\frac{2H(T_t - Q)}{l\sigma_t}\right]^{\frac{1}{2}}, \quad (2)$$

where, l is the thickness of a ceramic sample, $E_S = U_S/l$ is the average threshold electric intensity in a sample of ceramics; H is the specific coefficient of a thermal dispelling.

When electric intensity reaches E_S the switching takes place from a region 1 of voltage-current characteristic to a region 2 (Fig. 1). If we neglect by the contribution of VO_2 semiconductor phase in a full electric current through a sample, then the region 2 of VCC can be described in guess of cylindrical symmetry of channel (Fig. 2 à, a channel is shaded) by the expression:



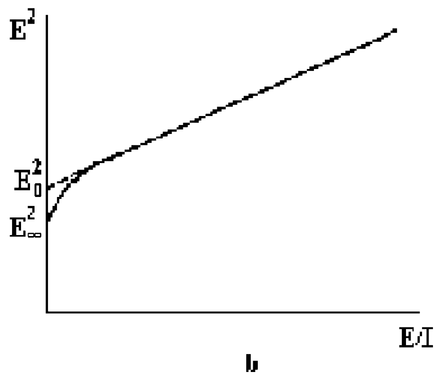


Fig. 2. The specimen shape (a) and the data of calculation for a region of voltage-current characteristic with negative differential conductivity in coordinates $E^2 \sim E/I$ (b).

$$I = \sigma_m E \pi R^2, \tag{3}$$

where, E is the average electric intensity in ceramics; R is the radius of channel of a current; σ_m is the effective conductivity of vanadium dioxide based ceramics when VO_2 crystal grains are in metal phase.

For given electric intensity E a balance between energy losses of electrical current in channel and energy dispelled in environment is determining a radius R.

For definition of the dependence of channel radius R from intensity of electric field E we shall consider the processes of a heat transfer in a thin cylindrical ceramic sample, exposed to an electrical current (Fig. 2a). The gradient of temperature in a direction of electric current (along axis Z in Fig. 2a) can be neglected for a thin samples. Let us accept also, that energy transmitted from a sample to an environment is proportional to a difference of temperatures $T-Q$ (T is the temperature in given point of surface of a sample, Q is an environmental temperature).

In a stationary case for a thin ring element dr of a sample (Fig. 2a) the energy balance will be defined by three contributions: $dW_1 = 2\pi\lambda l \frac{d}{dr}\left(r\frac{dT}{dr}\right)dtdr$—the energy delivered to a ring element during the time dt at heat transfer in radial direction; $dW_2 = 2\pi r\sigma E^2 ldtdr$—the energy delivered to an element by electric current; $dW_3 = 4\pi rH(T-Q)dtdr$—the energy dispersed during the time dt from a ring element to environment in direction normal to the surface of a sample (along axis Z in Fig. 2a). In this equation: l—thickness of a sample, r—radius of a ring element, λ—thermal conduction, σ—electrical conductivity, E—electric intensity, H—specific coefficient of a thermal dispelling.

If you take into account the balance of energy for a considered ring element dr ($dW_3 = dW_1 + dW_2$), it is possible to receive the following equation:

$$\frac{d^2T}{dr^2} + \frac{1}{r}\frac{dT}{dR} = \frac{2H}{l\lambda}\left((T-Q) - \frac{\sigma l E^2}{2H}\right) \tag{4}$$

We shall accept, that an environmental temperature Q is a constant. Then a variable $\Delta T = T-Q$ can be used in Eq. (4). If we use this equation for the description of heat transfer inside and outside the channel of electrical current, then the following equations can be received:

$$\frac{d^2\Delta T_m}{dr^2} + \frac{1}{r}\frac{d\Delta T_m}{dr} = \frac{2H}{l\lambda_m}\left(\Delta T_m - \frac{\sigma_m l E^2}{2H}\right) \tag{5}$$

$$\frac{d^2\Delta T_s}{dr^2} + \frac{1}{r}\frac{d\Delta T_S}{dr} = \frac{2H}{l\lambda_S}\Delta T_S, \tag{6}$$

here, $\Delta \dot{O}_m = T_m - Q$, $\Delta T_S = T_S - Q$ (T_m and T_S are the effective temperatures inside and outside the channel, accordingly); λ_m and λ_S are the effective thermal conductions of ceramic material inside and outside the channel, accordingly.

Eq. (5) describes a heat transfer in channel of electrical current containing VO_2 crystal grains in a metal phase. Eq. (6) describes a heat transfer in a part of a ceramic sample outside the channel, where VO_2 crystal grains are in semiconductor phase. In this equation we neglected the energy losses of electrical current, because $\sigma_S << \sigma_m$ (σ_S is the effective electrical conductivity of a ceramics at $T < T_t$). The boundary conditions for the Eqs. (5) and (6) are:

$$\text{at } r = 0 \qquad \frac{d\Delta T_m}{dr} = 0; \tag{7}$$

$$\text{at } r = R \qquad \Delta T_m = \Delta T_S = \Delta T_t = T_t\text{-}Q, \tag{8}$$

$$\lambda_m \frac{d\Delta T_m}{dr} = \lambda_S \frac{d\Delta T_S}{dr}. \tag{9}$$

The solution of Eq. (5) at the boundary conditions (7) and (8) gives such an expression:

$$\Delta T_m = \frac{\sigma_m l E^2}{2H} + \left(\Delta T_t - \frac{\sigma_m l E^2}{2H}\right)\frac{\sum_{k=0}^{\infty}\frac{1}{(k!)^2}\left(\frac{r}{R_0}\right)^{2k}}{\sum_{k=0}^{\infty}\frac{1}{(k!)^2}\left(\frac{R}{R_0}\right)^{2k}}. \tag{10}$$

The value R_0 in (10) is determined by expression:

$$R_0 = \left(\frac{2l\lambda_m}{H}\right)^{\frac{1}{2}}. \quad (11)$$

The solution of Eq. (6) can be obtained near the boundary of electric current channel in vicinity of a point $r=R$. If a coordinate r is represented as $r=R+x$, then at condition $x<<R$ Eq. (6) has a view:

$$\frac{d^2\Delta T_S}{dx^2} + \frac{1}{R}\frac{d\Delta T_S}{dx} = \frac{4\lambda_m}{\lambda_S R_0^2}\Delta T_S. \quad (12)$$

A solution of Eq. (12) at $\Delta T_S(0)=\Delta T_t$ and $x<<R$ gives:

$$\Delta T_S = \Delta T_t \exp[-(1+b)(r-R)/(2R)]. \quad (13)$$

where $b=[1+16(R/R_0)^2(\lambda_m/\lambda_S)]^{1/2}$.

Substitution (10) and (13) in the boundary condition (9) gives expression linking radius of a channel of electric current R with electric intensity E:

$$\frac{\sigma_m l}{H}\left(E^2 - \frac{2H\Delta T_t}{\sigma_m l}\right)\frac{\sum_{k=0}^{\infty}\frac{k}{(k!)^2}\left(\frac{R}{R_0}\right)^{2k}}{\sum_{k=0}^{\infty}\frac{1}{(k!)^2}\left(\frac{R}{R_0}\right)^{2k}} = \frac{\Delta T_t \lambda_S}{2\lambda_m}(1+b). \quad (14)$$

Let us analyse two boundary cases of very thin ($R/R_0<<1$) and of very wide ($R/R_0>>1$) channels of electrical current.

The restriction by one member of sum in (14) and by two members of a Taylor series of a value b is possible at $R/R_0<<1$. It gives:

$$R^2 = \frac{2\lambda_S\Delta T_t}{\sigma_m\left(E^2 - E_0^2\right)}, \quad (15)$$

where

$$E_0 = [6H\Delta T_t/(l\sigma_m)]^{1/2}. \quad (16)$$

The expressions (15) and (3) give:

$$I = \frac{2\pi\lambda_S\Delta T_t E}{E^2 - E_0^2}. \quad (17)$$

This expression describes the region of voltage-current characteristic which has the negative differential electrical resistance (region 2, Fig. 1). For this region of VCC the current is growing at decreasing of E, as it follow from (17). In accordance with (15) the reason of such behaviour is an expansion of channel of electric current.

The expression (17) can be written down as:

$$E^2 = E_0^2 + 2\pi\lambda_S\Delta T_t\frac{E}{I}. \quad (18)$$

Thus the region of VCC with a negative differential electric resistance must be linear in coordinates $E^2 \sim E/I$ at $R/R_0<<1$ (Fig. 2b). This linear plot intersects E^2 axis in a point corresponding by some value of electric intensity E_0. E_0 is the electric intensity in ceramic sample at unbounded increasing of a current. The value E_0 can be used for determination of effective conductivity σ_m. The slope of a linear region of dependence $E^2 \sim E/I$ can be used for determination of an effective thermal conduction of ceramics λ_S.

At $R/R_0>>1$ the expression for voltage-current characteristic in analytic form cannot be obtained. However, for the ceramic sample having unrestricted size in a radial direction r (Fig. 2a), it is possible to find the electric intensity E_∞ at unbounded increasing of a current. The value E_∞ can be obtained if in (14) the transition to the limit $R/R_0 \to \infty$ is made. This give the expression:

$$E_\infty = \left\{2H\Delta T_t\left[1+(\lambda_S/\lambda_m)^{1/2}\right]/(\sigma_m l)\right\}^{1/2}. \quad (19)$$

The value E_∞ is less than value of electric intensity E_0 obtained at $R/R_0<<1$. Therefore the dependence $E^2(E/I)$ at high currents must have a nonlinear behaviour. At unbounded increasing of electrical current the electric intensity in a ceramic sample will aspire not to the value E_0, but to the value E_∞ (Fig. 2b).

In Fig. 3 the region of voltage-current characteristic with negative differential conductivity in coordinates

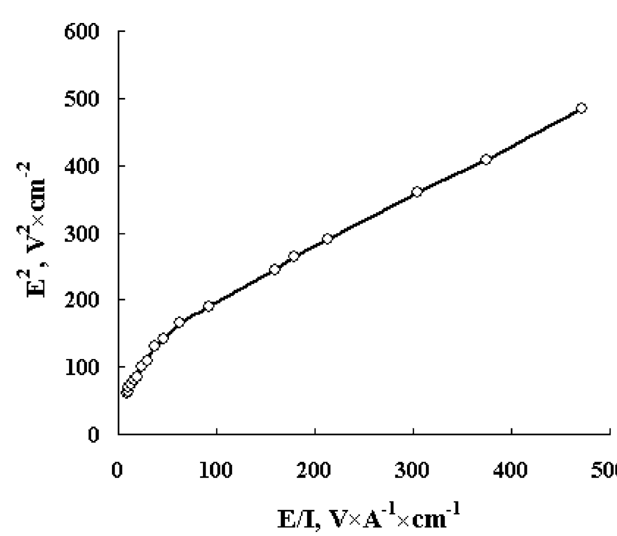


Fig. 3. The region of voltage-current characteristic with negative differential conductivity shown in coordinates $E^2 \sim E/I$, for ceramics (wt.%) 84VO_2–15VPG–1Cu.

$E^2 \sim E/I$ is given for ceramics of composition (wt.%) $84VO_2$-15VPG-1Cu. This dependence is linear in a region of nonlarge currents, when the condition $R/R_0 \ll 1$ is satisfied. It confirms correctness of the expression (17). For vanadium dioxide based ceramics the behaviour of dependence $E^2(E/I)$ in a region of high electrical currents, when condition $R/R_0 \gg 1$ is satisfied, also in conformity with behaviour which the expression (14) predicts (see Fig. 2b). However, let us note, as it follows from (3), the voltage-current characteristic becomes linear and will have positive differential conductivity when radius of a channel reaches the radius of a sample.

The content of copper has considerable influence on a voltage-current characteristic of vanadium dioxide based ceramics. As from data of Figs. 1 and 4 follows, an increasing of the content of copper gives lowering a threshold electric intensity E_S. As it follows from (2), such behaviour of E_S can be linked with increasing of effective conductivity of ceramics σ_t. The value of σ_t can be calculated using the value of voltage and current in a threshold point of a high-ohmic region of voltage-current characteristic of ceramics. In Fig. 5 the dependence $E_S(\sigma_t)$ in coordinates $E_S \sim (\sigma_t l)^{-1/2}$ is represented. The values of E_S are obtained from data of Figs. 1 and 4.

In these coordinates the experimental points lie down on a straight line which goes through the beginning of coordinates. It confirms applicability of model of "critical temperature"[5] for vanadium dioxide based ceramics and correctness of relation (2) at its usage for estimation of parameters of this ceramics on basis of experimental data.

In Fig. 6 the dependences $E^2(E/I)$ for vanadium dioxide based ceramics with different content of copper are shown. From these data follows, a slope of dependence $E^2(E/I)$ is increasing and the value of electric intensity E_0 is decreasing when the copper content grows. Table 1 gives the values of effective thermal conduction λ_S and conductivity σ_m which are calculated using the formulas (2), (16) and (18) on basis of experimental results represented above. Table 1 also contains the values of effective electrical conductivity of ceramics: σ_S is obtained from ohmic region of voltage-current characteristic; σ_t is calculated at a threshold point of VCC; σ_m^{ex} is obtained by a direct method of measurement of electrical conductance of ceramics at the temperature 100°Ñ.

From the table data it follows, the increase of copper content in vanadium dioxide based ceramics gives an increase of effective thermal conduction λ_S and conductivities below (σ_S) and above (σ_m) of the phase transition temperature T_t. It is necessary to mark good

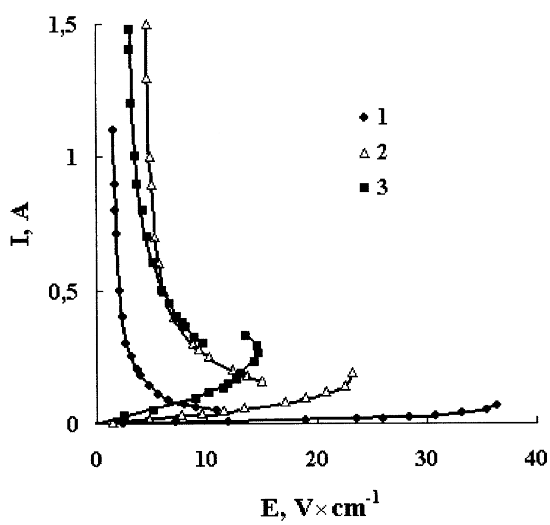


Fig. 4. Voltage-current characteristics of vanadium dioxide based ceramics with different content of copper (wt.%): 1—$83VO_2$–15VPG–2Cu; 2—$81VO_2$–15VPG–4Cu; 3—$80VO_2$–15VPG–5Cu.

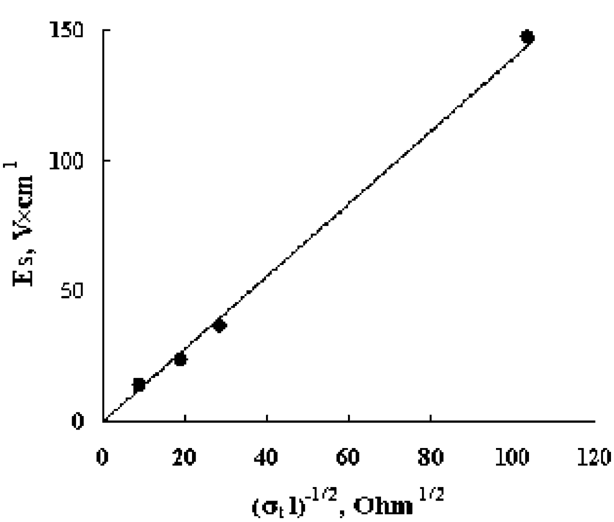


Fig. 5. Threshold electric intensity E_S in coordinates $E_S \sim (\sigma_t l)^{-1/2}$ for vanadium dioxide based ceramics of different composition.

Table 1
Some electrical and heat parameters of vanadium dioxide based ceramics with the different content of copper

The composition of ceramics (wt.%)	σ_S Ohm^{-1} cm^{-1} (T=20 °C)	σ_t Ohm^{-1} cm^{-1}	λ_S Wt/(K cm)	σ_m Ohm^{-1} cm^{-1}	σ_m^{ex} Ohm^{-1} cm^{-1} (T=100 °C)
$84VO_2$–15VPG–1Cu	$1.54 \cdot 10^{-4}$	$5.20 \cdot 10^{-4}$	$2.33 \cdot 10^{-3}$	0.36	0.32
83 VO_2–15VPG–2Cu	$2.01 \cdot 10^{-3}$	$5.77 \cdot 10^{-3}$	$1.56 \cdot 10^{-3}$	3.82	2.51
81 VO_2–15VPG–4Cu	$1.15 \cdot 10^{-2}$	$2.71 \cdot 10^{-2}$	$7.21 \cdot 10^{-3}$	8.77	10.3
80 VO_2–15VPG–5Cu	$2.54 \cdot 10^{-2}$	$6.39 \cdot 10^{-2}$	$8.31 \cdot 10^{-3}$	11.81	12.5

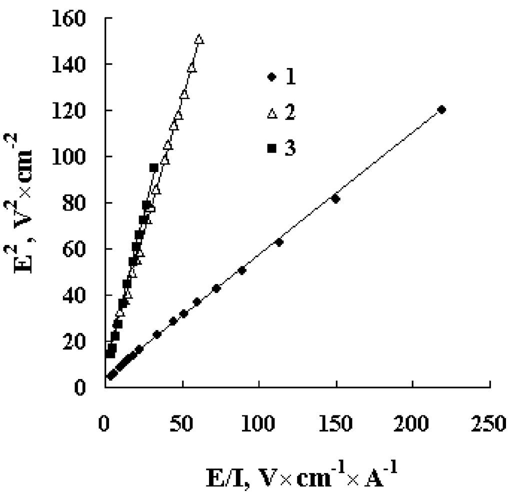


Fig. 6. The regions of voltage-current characteristic with negative differential conductivity in coordinate $E^2 \sim E/I$ for ceramics of composition (wt.%): 1—83VO_2–15VPG–2Cu; 2—81VO_2–15VPG–4Cu; 3—80VO_2–15VPG–5Cu.

correspondence between the value of the effective conductivity obtained by calculation σ_m and the value of the conductivity σ_m^{ex} measured for ceramics at $T > T_t$. Let us mark also correspondence between the values of thermal conduction measured by authors[10] ($\lambda_S \approx 2 \cdot 10^{-3}$ Wt K^{-1} sm^{-1}) for composite consisting of crystalline powder of VO_2 and small amount of polymeric filling compound (no more than 3 wt.%) and obtained by us for ceramics with the content of copper no more than 2 wt.%. The increase of effective thermal conduction and electrical conductivity of vanadium dioxide based ceramics at the increase of copper content is probably linked to two reasons. Firstly, a copper in ceramics is present as an inclusions, which give complementary electrical and thermal contacts between VO_2 crystal grains. Secondly, a microstructure of ceramics changes with change of contents of a copper additive. According to the data of our preliminary investigations, the increasing of copper content gives a decrease of the sizes of VO_2 crystal grains and decreases the porosity of ceramics. Therefore a material with copper additive is more dense and has more highly effective electrical conductivity and thermal conduction.

Thus, according to the results introduced above we can conclude, that the additive of copper considerably influences electrical and thermal properties of vanadium dioxide based ceramics. This additive can be used for control by the electrical parameters and characteristics of this material.

4. Conclusions

The vanadium dioxide based ceramics has a voltage-current characteristic of S-type with a threshold of switching. Ceramics can pass an electrical current up to several amperes in low ohmic state. Below a threshold of switching, the temperature of the ceramic sample does not exceed the temperature T_t of the metal-semiconductor phase transition in vanadium dioxide, therefore all crystal grains of VO_2 are in a semiconductor phase. When the threshold of switching is reached the voltage current characteristic of ceramics is determined by the channel of an electrical current with crystal grains of VO_2 in a metal phase. The analytical expression for a voltage-current characteristic of the ceramic sample with the channel of cylindrical shape is obtained. This expression correctly describes the results of the experiment.

The values of effective conductivity σ_m ($T > T_t$) and effective thermal conduction λ_S ($T < T_t$) of vanadium dioxide based ceramics with different content of copper are calculated using the low ohmic region of voltage current characteristic. The values of σ_m and λ_S are increasing and a voltage of switching is decreasing as the copper content increases. The possible reason of such behaviour of σ_m and λ_S can be connected with an increasing of the amount of electrical and thermal bonds between VO_2 crystal grains through the inclusions of copper, and also with the decrease in porosity of ceramics.

The additive of copper can be used for the control by electric parameters of vanadium dioxide based ceramics.

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