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INFLUENCE OF COPPER ON ELECTRICAL CONDUCTIVITY OF GLASS-CERAMICS BASED ON VANADIUM DIOXIDE

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The results of studying the electrical conductivity σ for the glass-ceramic systems VO_2–vanadium-phosphate glass (VPG) and VO_2–VPG–SnO_2 with the additions of Cu and Cu_2O are presented. It is found that the jump of conductivity at the temperature of metal-semiconductor phase transition (MSPT) in VO_2 (T_t = 341K) takes place only for glass-ceramics containing not more than 5 wt% of these additives. When their content exceeds 5 wt%, the VO_2 content decreases sharply according to the data of differential thermal analysis. The reason for this is the oxidation-reduction reactions in the liquid phase between Cu and VO_2 at ceramics synthesis. These reactions result in the appearance of Magneli phases in glass–ceramics composition. The phase transitions in Magneli phases V_4O_7, V_5O_9, and V_6O_{13} are indicated by the temperature dependence of σ, as bends of the straight lines in coordinates $\log_{10}\sigma \sim 1/T$ at the phase transition temperatures T_t of these phases: 240K, 150K, and 130K. The activation energy of σ for T> Tt is lower than for T <Tt, which indicates a change in the structure of energy zones inherent to MSPT.

Keywords: glass-ceramics, electrical conductivity, metal-semiconductor phase transition, vanadium dioxide, Magneli phases.

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1. Introduction

Glass-ceramic materials based on vanadium dioxide (VO_2) – vanadium-phosphate glass (VPG) system have the abrupt change in electrical conductivity near the temperature T_t = 341K. This change is 2-3 orders of magnitude and is a consequence of the metal-semiconductor phase transition (MSPT) in VO_2 [1]. This allows using such materials in critical thermistors that combine the properties of a conventional thermistor with a negative temperature coefficient of resistance and a thermal relay. Such thermistors can be used to protect power supplies and incandescent lamps from turn-on currents effectively [2, 3]. The electrical conductivity σ of glass-ceramics in the VO_2–VPG system and the magnitude of the jump σ in the region of MSPT in VO_2 can be controlled by the additives of copper, Cu_2O and tin dioxide SnO_2 [1, 4]. It is shown in [4], that at the synthesis of glass-ceramics in VO_2–VPG–SnO_2 system, the VPG in a liquid phase is chemically neutral to VO_2 and SnO_2. According to the data of scanning electron microscopy and X-ray phase analysis [1, 4], the glass-ceramics of VO_2–VPG system contains VO_2 crystallites, and the glass-ceramics of VO_2–VPG–SnO_2 system contains VO_2 and SnO_2 crystallites. VO_2 crystallites have sizes from 3.5 to 50 μm, and SnO_2 crystallites have sizes from 5 to 17 μm. VPG forms layers with the thickness of 1-2 microns in the space between crystallites. Vanadium dioxide dissolves in the liquid phase at glass-ceramics synthesis, which contributes to the growth of its crystallites.

The introduction of Cu and Cu_2O into the VO_2–VPG and VO_2–VPG–SnO_2 systems significantly changes the electrical conductivity, phase composition, and microstructure of glass-ceramics. In its X-ray spectra the lines appear that were identified by JCPDS files as Magneli phases: V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, V_4O_9, V_6O_{13} [4]. The intensity of the VO_2 lines in X-ray spectra decreases when Cu and Cu_2O contents grow. Such behavior of VO_2 lines and the appearance of Magneli phases indicate a chemical interaction between copper and vanadium dioxide at the synthesis of glass-ceramics. Since according to the data of X-ray microanalysis, Cu and VO_2 dissolve in the liquid phase, such interaction may be a consequence of oxidation-reduction reactions between them. This is confirmed by the appearance of CuO lines in the X-ray spectra of glass-ceramics after its synthesis [4]. As is known [5], at low temperatures the Magneli phases have MSPT with a jump of electrical conductivity. This transition is associated with a change in the structure of energy zones and it can give a contribution to the low-temperature electrical conductivity of VO_2 based glass-ceramics with the additions of Cu and Cu_2O. In this connection, the aim of this work is to study the electrical conductivity of glass-ceramics in systems VO_2–VPG and VO_2–VPG–SnO_2 with the additives of Cu and Cu_2O in a wide temperature range.

2. Samples and methods of investigation

The vanadium-phosphate glass of composition (mol.%) $80V_2O_5$–$20P_2O_5$ and VO_2 are the basic components of glass-ceramics. Vanadium-phosphate glass was obtained according to the technology described in [6]. Crystalline vanadium dioxide was obtained by means of V_2O_5 reducing with carbon in a neutral gas atmosphere [7]. [1, 4] describe the technology that was used for producing glass-ceramic samples $(85–\alpha)VO_2$–15VPG–αCu with α in the range of 0 wt% $\le \alpha \le$ 15 wt% and $40VO_2$–15VPG–αCu_2O–$(45 - \alpha)$ SnO_2 with α in the range of 0 wt% $\le \alpha \le$ 10 wt%.

Samples for studying the temperature dependence of electrical conductivity had a disk shape with a base diameter of 10 mm and a thickness of 2 mm. Electrodes for the samples were created by copper electrodeposition.

The temperature dependence of electrical conductivity at low temperatures was measured in an alcohol cryostat at heating rate of the test sample not more than 1 K/min. Measurements in the temperature range 290 K – 400 K were performed in an electric furnace with heating rate not more 1.5 K/min. For temperature measurements with an absolute error no more than ±0.5 K the copper resistance thermometer was used. The sample resistance was measured with a relative error of ±1% by means of a direct-current bridge MO-62.

The data of differential thermal analysis (DTA) were used for the measurement of VO_2 content in studied glass-ceramics according to the method described in [8]. The VO_2 content was determined by comparing the areas of endothermic peaks in DTA curves near the temperature 341K for the glass-ceramics and vanadium dioxide crystals. DTA measurements were performed on instrument OD-103A in the temperature range 290 K – 420 K at a heating rate of 1.25 K/min.

2. Experimental results and discussion

Fig. 1 shows the temperature dependences of the specific conductivity σ for glass-ceramics $40VO_2$–15VPG–αCu_2O–$(45 - \alpha)SnO_2$ with different content of Cu_2O. As it can be seen, the jump of conductivity at 341K, associated with the MSPT in VO_2, is observed only for compositions containing no more than 5 wt% Cu_2O. In compositions with Cu_2O content of 8 wt% or more, such jump is absent. The reason for this may be the absence of percolation through VO_2 phase due to its low content. This is confirmed by the Fig. 2, which shows the dependences of the VO_2 content in the mixture for the manufacture of glass-ceramic (wt%) $(85 - \alpha)VO_2$–15VPG–αCu before (curve 1) and after (curve 2) ceramics synthesis. It is follows from Fig. 2 data, that the content of vanadium dioxide in glass-ceramics sharply decreases when the content of Cu additive exceeds 5 wt%. When the content of Cu is 15 wt%, the VO_2 content does not exceed 1.5 wt%. A decrease in the VO_2 content with an increase in the copper content is probably a consequence of the oxidation-reduction reactions between these components, since the liquid phase at the ceramics synthesis contains dissolved VO_2 and Cu. This is confirmed by the appearance of the CuO lines in X-ray spectra of glass-ceramics when the content of Cu_2O exceeds 7 wt% [4]. As the result of the reaction $nVO_2 + Cu \rightarrow V_nO_{2n-1} + CuO$, the Magneli phases with the general formula V_nO_{2n-1} may crystallize in the liquid phase during the glass-ceramics synthesis. The presence of such phases in ceramics on the basis of VO_2 with a high copper content was confirmed by X-ray phase analysis [4].

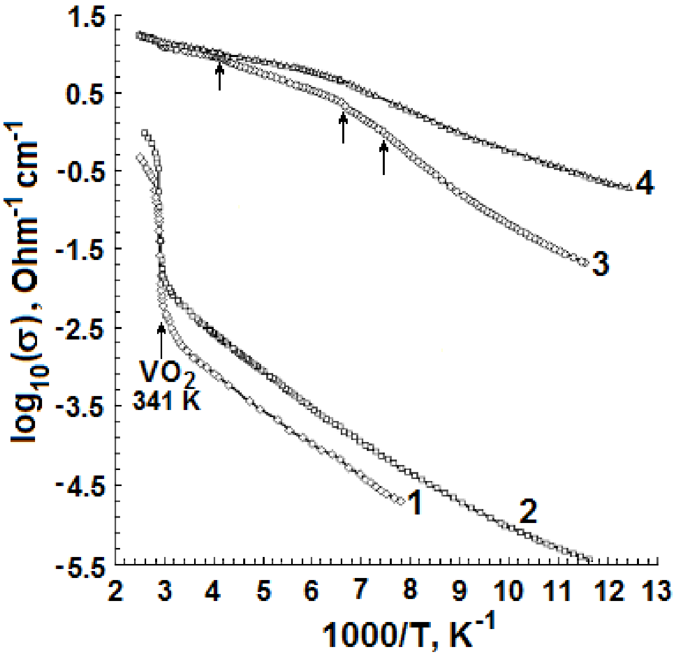

Fig. 1. Temperature dependences of the specific electrical conductivity of glass-ceramics $40VO_2$–15VPG–αCu_2O–$(45–\alpha)SnO_2$ with Cu_2O content α (wt%): 1 – 2; 2 – 5; 3 – 8; 4 – 10.

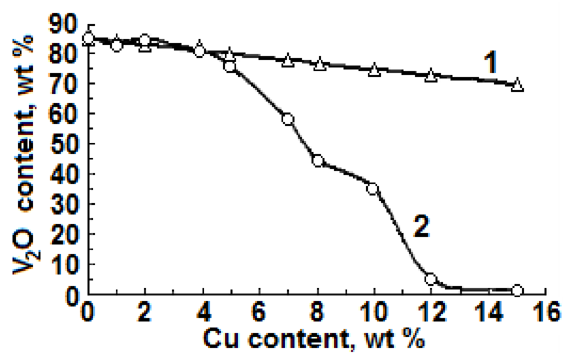

Fig. 2. Dependence of VO_2 content on copper content α for glass-ceramics $(85–\alpha)VO_2$–15VPG–αCu in the initial mixture (1) and after synthesis (2)

The values of the MSPT temperature T_t for some phases of Magneli, according to different authors, are shown in the Tab. 1.

Table 1

Metal-semiconductor phase transition temperature for some vanadium oxides

Compound	Temperature of MSPT T_t, K	Change in conductivity at MSPT temperature [5]
VO_2	340 [5]	10^5
V_3O_5	450 [5],	10^2
V_4O_7	240 [5], 237 [9]	10^3, 10^2 [9]
V_5O_9	130 [5], 129 [11]	10^6
V_6O_{13}	150 [5], 153 [10]	10^6

As it can be seen in Fig. 1, a significant increase in electrical conductivity σ takes place with increasing Cu_2O content in ceramics $40VO_2$–15VPG–αCu_2O–$(45 - \alpha)SnO_2$. The temperature dependence σ in the Arrhenius coordinates for the samples with a high Cu content shows bends for the straight line in coordinates $\log_{10}\sigma \sim 1/T$ at certain temperatures (temperatures are indicated by arrows in Fig. 1). These bends show a transition from higher values of activation energy to lower values with temperature increasing. This behavior is not typical for semiconductor materials, the electrical conductivity of which is determined by donor or acceptor levels, and indicates a change in the energy structure of zones at temperatures corresponding to the bends. As it is known [5], a change in energy structure of zones occurs at the metal-semiconductor phase transitions. For such transitions at the temperature of MSPT T_t, the character of temperature behavior of electrical conductivity changes from the activation behavior to the metallic behavior with temperature increasing. This is accompanied by a sharp increase in electrical conductivity.

It follows from the data in Fig. 1 that the glass-ceramics with composition $40VO_2$–15VPG–$8Cu_2O$–$37SnO_2$ shows the most evident bends of the linear dependence $\log_{10}\sigma \sim 1/T$. In Fig. 3 the temperature dependences of electric conductivity for this ceramics are shown in the Arrhenius coordinates in the region of the bend temperatures. Table 2 shows the activation energies of σ below and above the temperature corresponding to a bend in the dependence $\log_{10}\sigma \sim 1/T$.

Table 2

The activation energy of electrical conductivity for glass-ceramics (wt%) $40VO_2$–15VPG–$8Cu_2O$–$37SnO_2$ in the temperature range of the bend in dependence on $\log_{10}\sigma \sim 1/T$

Magneli phase	V_4O_7		V_6O_{13}		V_5O_9	
Temperature range, K	T > 240	T < 240	T > 150	T < 150	T > 130	T < 130
Activation energy, eV	0.021	0.041	0.042	0.084	0.082	0.106

As it can be seen, taking into account Tab. 1, the temperatures at which a change in activation energy of electrical conductivity takes place correspond to the temperatures of MSPT in Magneli phases V_4O_7, V_6O_{13}, and V_5O_9. For the V_4O_7 phase, in addition to the transition from higher to lower activation energy near $T_t \sim 240$ K, an enough pronounced sharp increase in the electrical conductivity is observed with the temperature increasing. This is typical for the metal-semiconductor phase transition (Fig. 3a). The presence of the contribution of Magneli phases to the electrical conductivity of glass-ceramics on the basis of VO_2 with a high copper content (8 wt% or more) indicates that their volume fraction exceeds the percolation threshold. For small additions of Cu, there is no percolation through the Magneli phases and vanadium dioxide provides the main contribution to the electrical conductivity of glass-ceramics.

Thus, the above results and the data of X-ray phase analysis [4] confirm that oxidation-reduction reactions in the liquid phase lead to the crystallization of Magneli phases during the ceramic synthesis in systems VO_2–VPG and VO_2–VPG–SnO_2 with Cu and Cu_2O additives. These phases for small additives of copper (up to 5 wt%) are located in the layers of VPG separating VO_2 crystallites. Since the Magneli phases in the Tab. 1 go into a conductive state at temperatures substantially lower than the temperature of the MSPT in VO_2, they create conductive bonds between VO_2 crystallites above 240 K. The developed network of such conductive bonds promote the percolation of electric current through VO_2 crystallites ensuring their decisive contribution into electrical properties of glass-ceramics and increasing ceramics stability during thermocycling through the temperature of MSPT in vanadium dioxide.

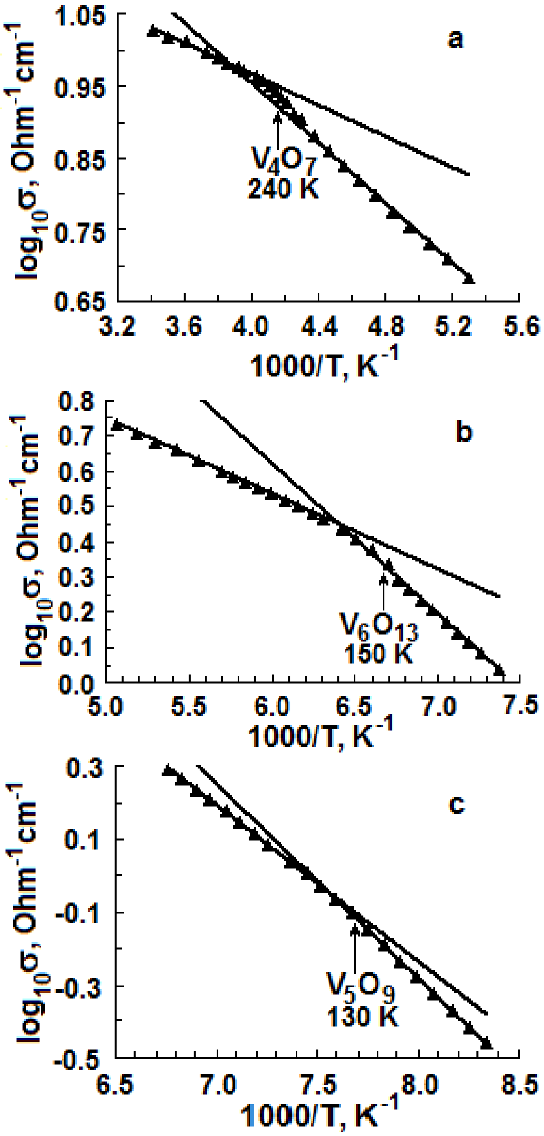

Fig. 3. Temperature dependences of the electrical conductivity of glass-ceramics (wt%) $40VO_2$–15VPG–$8Cu_2O$–$37SnO_2$ near the temperature of metal-semiconductor phase transition in Magneli phases: a – V_4O_7; b – V_6O_{13}; c – V_5O_9

3. Conclusions

The electrical conductivity σ of glass-ceramics in the systems VO_2–VPG and VO_2–VPG–SnO_2 with the additives of Cu and Cu_2O is studied in the temperature range 77 K – 400 K.

It is found that a jump of σ near the temperature T_t = 341K of the metal-semiconductor phase transition in VO_2 is observed only for glass-ceramic compositions containing no more than 5 wt% of these additives. When their content exceeds 5 wt%, the VO_2 content decreases sharply according to the data of differential thermal analysis. The reason for this is the oxidation-reduction reactions between Cu and VO_2 in the liquid phase at ceramics synthesis. These reactions result in the appearance of Magneli phases in glass-ceramics composition. The phase transitions in Magneli phases V_4O_7, V_5O_9, and V_6O_{13} are detected by the temperature dependence of σ as bends of the straight line in coordinates $\log_{10}\sigma \sim 1/T$ at the temperatures of MSPT in these phases: 240K, 150K and 130K. The activation energy of conductivity for $T > T_t$ is lower than for $T < T_t$, that indicates in a change of the energy structure of zones to the typical for the metal-semiconductor phase transition.

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