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

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The results of studying the electrical conductivity $\sigma$ for the glass-ceramic systems VO$_2$–vanadium-phosphate glass (VPG) and VO$_2$–VPG–SnO$_2$ with the additions of Cu and Cu$_2$O are presented. It is found that the jump of conductivity at the temperature of metal-semiconductor phase transition (MSPT) in VO$_2$ ($T_t = 341$K) 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$_2$O$_5$, V$_3$O$_8$, and V$_6$O$_{12}$ are indicated by the temperature dependence of $\sigma$, as bends of the straight lines in coordinates $\log(\sigma) = 1/T$ at the phase transition temperatures $T_1$ of these phases: 240K, 150K, and 130K. The activation energy of $\sigma$ for $T > T_t$ is lower than for $T < T_t$, 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 $T_t = 341$K. This change is 2-3 orders of magnitude and is a consequence of the metal-semiconductor phase transition (MSPT) in VO$_2$. 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 $\sigma$ of glass-ceramics in the VO$_2$–VPG system and the magnitude of the jump $\sigma$ in the region of MSPT in VO$_2$ can be controlled by the additives of copper, Cu$_2$O 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 $\mu$m, and SnO$_2$ crystallites have sizes from 5 to 17 $\mu$m. 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$_2$O 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$_2$O$_5$, V$_3$O$_8$, V$_6$O$_{13}$, V$_4$O$_9$, V$_8$O$_{12}$ [4]. The intensity of the VO$_2$ lines in X-ray spectra decreases when Cu and Cu$_2$O 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

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it can give a contribution to the low-temperature electrical conductivity of VO₂ based glass-ceramics with the additions of Cu and Cu₂O. In this connection, the aim of this work is to study the electrical conductivity of glass-ceramics in systems VO₂–VPG and VO₂–VPG–SnO₂ with the additives of Cu and Cu₂O in a wide temperature range.

2. Samples and methods of investigation

The vanadium-phosphate glass of composition (mol.%) 80V₂O₅–20P₂O₅ and VO₂ 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 V₂O₅ reducing with carbon in a neutral gas atmosphere [7]. [1, 4] describe the technology that was used for producing glass-ceramic samples (85–α)VO₂–15VPG–αCu with α in the range of 0 wt% ≤ α ≤ 10 wt% and 40VO₂–15VPG–αCu₂O–(45–α)SnO₂ with α in the range of 0 wt% ≤ α ≤ 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 VO₂ content in studied glass-ceramics according to the method described in [8]. The VO₂ 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 40VO₂–15VPG–αCu₂O–(45–α)SnO₂ with different content of Cu₂O. As it can be seen, the jump of conductivity at 341K, associated with the MSPT in VO₂, is observed only for compositions containing no more than 5 wt% Cu₂O. In compositions with Cu₂O content of 8 wt% or more, such jump is absent. The reason for this may be the absence of percolation through VO₂ phase due to its low content. This is confirmed by the Fig. 2, which shows the dependences of the VO₂ content in the mixture for the manufacture of glass-ceramic (wt%) (85 – α)VO₂–15VPG–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 VO₂ content does not exceed 1.5 wt%. A decrease in the VO₂ 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 VO₂ and Cu. This is confirmed by the appearance of the CuO lines in X-ray spectra of glass-ceramics when the content of Cu₂O exceeds 7 wt% [4]. As the result of the reaction nVO₂ + Cu → VₙO₂ₙ₋₁ + CuO, the Magneli phases with the general formula VₙO₂ₙ₋₁ may crystallize in the liquid phase during the glass-ceramics synthesis. The presence of such phases in ceramics on the basis of VO₂ with a high copper content was confirmed by X-ray phase analysis [4].

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Fig. 1. Temperature dependences of the specific electrical conductivity of glass-ceramics 40VO₂–15VPG–αCu₂O–(45–α)SnO₂ with Cu₂O content α (wt%): 1 – 2; 2 – 5; 3 – 8; 4 – 10.

Fig. 2. Dependence of VO₂ content on copper content α for glass-ceramics (85–α)VO₂–15VPG–αCu in the initial mixture (1) and after synthesis (2).

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature of MSPT Tᵣ, K</th>
<th>Change in conductivity at MSPT temperature [5]</th>
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<tbody>
<tr>
<td>VO₂</td>
<td>340 [5]</td>
<td>10³</td>
</tr>
<tr>
<td>V₅O₉</td>
<td>150 [5], 153 [10]</td>
<td>10⁶</td>
</tr>
<tr>
<td>V₆O₁₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As it can be seen in Fig. 1, a significant increase in electrical conductivity $\sigma$ takes place with increasing Cu$_2$O content in ceramics $40$VO$_2$–$15$VPG–$\alpha$Cu$_2$O–$(45 - \alpha)$SnO$_2$. The temperature dependence $\sigma$ 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 $40$VO$_2$–$15$VPG–$8$Cu$_2$O–$37$SnO$_2$ 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 $\sigma$ below and above the temperature corresponding to a bend in the dependence $\log_{10}\sigma \sim 1/T$.

### Table 2

<table>
<thead>
<tr>
<th>Magneli phase</th>
<th>$\text{V}_4\text{O}_7$</th>
<th>$\text{V}<em>6\text{O}</em>{13}$</th>
<th>$\text{V}_5\text{O}_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature range, K</td>
<td>$T &gt; 240$</td>
<td>$T &lt; 240$</td>
<td>$T &gt; 150$</td>
</tr>
<tr>
<td>Activation energy, eV</td>
<td>0.021</td>
<td>0.041</td>
<td>0.042</td>
</tr>
</tbody>
</table>

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 $\text{V}_4\text{O}_7$, $\text{V}_6\text{O}_{13}$, and $\text{V}_5\text{O}_9$. For the $\text{V}_4\text{O}_7$ phase, in addition to the transition from higher to lower activation energy near $T_t \approx 240$ 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$_2$O 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 promotes the percolation of electric current through VO$_2$ crystallites ensuring their decisive contribution into electrical properties of
The electrical conductivity $\sigma$ of glass-ceramics in the systems $\text{VO}_2$–$\text{VPG}$ and $\text{VO}_2$–$\text{VPG}$–$\text{SnO}_2$ with the additives of Cu and $\text{Cu}_2\text{O}$ is studied in the temperature range 77 K–400 K.

It is found that a jump of $\sigma$ near the temperature $T_i = 341$K of the metal-semiconductor phase transition in $\text{VO}_2$ is observed only for glass-ceramic compositions
containing no more than 5 wt% of these additives. When their content exceeds 5 wt%, the VO₂ content decreases sharply according to the data of differential thermal analysis. The reason for this is the oxidation-reduction reactions between Cu and VO₂ in the liquid phase at ceramics synthesis. These reactions result in the appearance of Magnéli phases in glass-ceramics composition. The phase transitions in Magnéli phases V₄O₇, V₅O₉, and V₆O₁₃ are detected by the temperature dependence of σ as bends of the straight line in coordinates log₁₀σ ~ 1/T at the temperatures of MSPT in these phases: 240K, 150K and 130K. The activation energy of conductivity for T > Tᵣ is lower than for T < Tᵣ, that indicates in a change of the energy structure of zones to the typical for the metal-semiconductor phase transition.

References