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THERMAL BEHAVIOR OF DISPERSED VANADIUM DIOXIDE PARTICLES IN POLYETHYLENE GLYCOL MATRIX CONTAINING TETRAETHYLAMMONIUM BROMIDE

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Abstract

A study has been made on samples of dispersed vanadium dioxide (VO_2) in a matrix of polyethylene glycol (PEG) doped with a quaternary ammonium salt (QAS), namely tetraethylammonium bromide. It has been established that under the influence of the dopant the heating of a sample up to the temperature of the metal-semiconductor phase transition (MSPT) results in a phase inhomogeneity of the sample. On the basis of the results of this study it is possible to conclude that small concentrations of QAS in a PEG matrix can exert a strong effect on the electronic structure of dispersed VO_2 particles. This is accompanied by the appearance of phase heterogeneity of VO_2 which manifests itself in the fact that – with the onset of MSPT with increasing temperature – one portion of the substance passes into the metallic state, and the other remains in the semiconductive state.

Keywords: metal-semiconductor phase transitions, NMR, polyethylene glycol matrix, vanadium dioxide

Introduction

Vanadium dioxide (VO_2) is a typical representative of substances with a metal-semiconductor phase transition. The phase transition temperature is 340 K. As a result of the phase transition (PT) the sample conductivity changes by several orders of magnitude [1].This property of vanadium dioxide allows one to use it in a number of devices of electrical, radio, and microwave engineering [2]. In this case, one of the ways to expand functional capabilities of the material is the development of methods for the control over its phase transition temperature.

Today it is known that the MSPT temperature may change because of emergence of an electric charge on the VO_2 surface. Such a charge may appear during surface adsorption of some types of active molecules, in particular molecules of water and ammonia [3–5], as well as during interactions of VO_2 particles with a polymeric matrix [6, 7]. These types of interactions can decrease the PT temperature down to 320 K. However, the search for new systems that would make it possible to vary the PT temperature sufficiently quickly and reversibly in a wider temperature interval re-

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mains an urgent problem. In our opinion, one of the promising directions of studies in this field is an approach involving the application of permeable polymeric matrices that are able to absorb some molecules and, as a result, to exert an effect upon the electronic structure of dispersed vanadium dioxide particles through variations of the charge state of their surface.

Experimental

Polyethylene glycol (PEG) with a molecular mass of 1500 was chosen as a polymeric matrix. The melting temperature of this substance is 310 K, therefore at temperatures near to the PT temperature for VO_2 its state is close to that of a very viscous liquid. PEG is able to absorb a considerable amount of water. Besides, it can dissolve many organic compounds.

Dispersed powders of VO_2 were prepared by the solid phase synthesis [7]. The research was carried out by the ^{1}H NMR spectroscopy [5, 8]. By means of this technique MSPT in suspensions and polymeric matrices can be recorded by applying a contactless method in terms of variations of spectral characteristics of the proton signal from molecules of the polymer, suspending medium or substances adsorbed on the dispersed VO_2 particle surface. This method of measurements is based on the fact that upon a sharp change of the sample conductivity one can observe an increase in the concentration of free electrons which induce paramagnetic relaxation of nuclear spins of protons of molecules contiguous to the VO_2 particle surface. It results in a broadening of the NMR signals and decreasing of their intensity, which is caused by absorption of electromagnetic energy in the sample.

Results and discussion

Figure 1 illustrates the temperature-induced variations of the ^{1}H NMR spectra for VO_2 in PEG as well as the temperature dependence of the proton signal intensity (I). In these spectra there is a broad single peak that is an average signal for protons of CH and OH groups of PEG and of impurity water molecules adsorbed on the VO_2 surface and in the bulk of PEG. As the temperature approaches the PT temperature value, the width of the signal sharply increases, and its intensity decreases by about 40%, which allows reliable recordings of the PT occurrence in the system. The function $I=f(T)$ shows a hysteresis characteristic of dispersed samples of VO_2 [6, 7].

Figure 2 shows the temperature dependence of the ^{1}H NMR signal intensity for VO_2 whose water content is 10 mass% in a PEG matrix. A comparison between the data of Figs 2 and 1b permits us to conclude that, in contrast to the case of hydrated VO_2 powders, MSPT in a PEG medium vary slightly, when the moisture content of a sample increases. It is attributed to the fact that molecules of PEG interact with molecules of water through the formation of hydrogen-bonded associates. As they penetrate into the bulk of the polymer, molecules of water do not adsorb on the VO_2 particle surface but reside within the polymeric matrix.

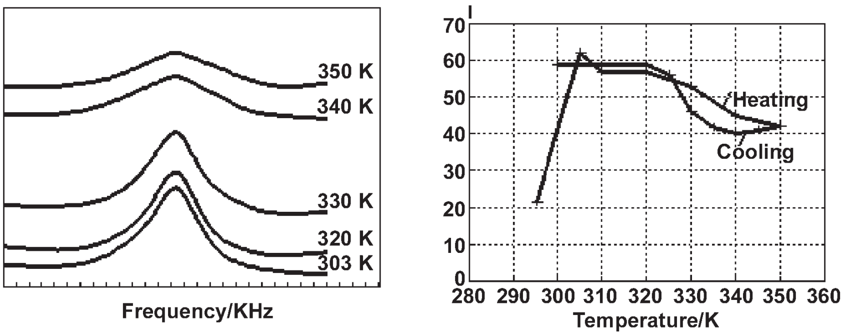

Fig. 1 Temperature-induced variations of the ^{1}H NMR spectra shape and signal intensity for protons in VO_2 powders in a PEG matrix

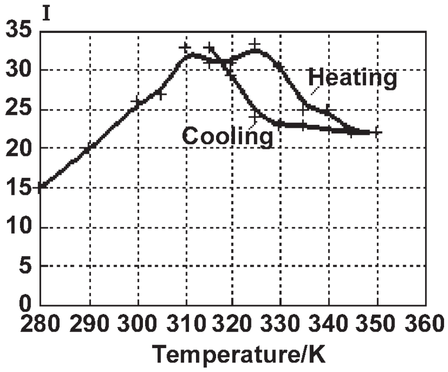

Fig. 2 Temperature dependence of variations of the ^{1}H NMR signal intensity for a sample of VO_2 containing 10 mass% of water in a PEG medium

In the capacity of a modifying dopant capable of exerting an effect on the VO_2 surface we have tested a quaternary ammonium salt (QAS), namely tetraethylammonium bromide. Some media with a low dielectric permeability, which include polyethylene glycol, can carry quaternary ammonium salts in the form of tight ionic pairs. Because of the great difference in sizes of anionic and cationic components of a molecule their mobilities differ considerably. In the viscous PEG medium this difference should be even greater on account of the strong dispersion interaction between ethyl groups of the $(C_2H_5)_4N^+$ cation and molecules of the polymer. In view of this, it could be expected that cationic and anionic components of QAS molecules would interact with the VO_2 surface in different ways and give rise to its polarization.

Figures 3a, b display temperature variations of the ^{1}H NMR spectra for VO_2 in the PEG medium containing small (<1%) additives of QAS. As is evident from the figure, at heating up to temperatures lower than the MSPT temperature the shape of the spectrum peaks is similar to that of the spectrum in Fig. 1. PT occurs at a temperature of 335 K. It manifests itself in a broadening of the signal width and lowering of its intensity. At the same time, however, in the background of the main signal, a signal of a lower intensity

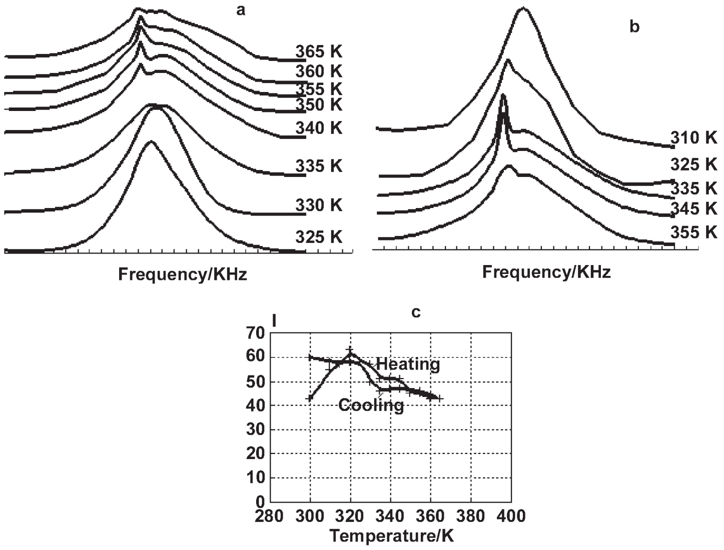

Fig. 3 Temperature-induced variations of the ^{1}H NMR spectra shape for a sample of VO_2 in a PEG matrix (a, b) and ^{1}H NMR signal intensity (c) containing an additive of tetraethylammonium bromide

appears the width of which is substantially smaller than that of the main signal. The width of this signal does not practically vary in the temperature interval $340<T<360$ K. At higher temperatures its width increases. The presence of the second signal in the spectra is observed even more distinctly under cooling of a sample. In this case the second signal in the spectra is not detected only at temperatures of $T>310$ K.

Figure 3c presents curves of the relationship $I=f(T)$ for a sample containing a QAS additive. In comparison with the dependence plotted in Fig. 1, this relationship exhibits several particularities. One of them is the appearance of practically horizontal segments in the temperature interval $335<T<345$ K.

The results achieved can be interpreted as follows. In the case of dispersed VO_2 powders the presence of QAS in a PEG matrix causes formation of zones on the VO_2 particle surface, where the MSPT temperature is shifted into a higher temperature region. Within these zones PT is observed only when the temperature reaches the value of $T=365$ K. The phenomenon detected is the first example of the increase in the MSPT temperature under the action of external factors and, to a certain extent, is similar to the widely known intermediate state of a superconductor in a magnetic field [9].

As it was mentioned, the reason for the changes in the MSPT temperature may be the emergence of an electric field near the surface, that is assigned to polarization of molecules of an adsorbed substance [3]. In particular, at surface adsorption of electron-donating molecules of ammonia and water the VO_2 surface acquires a positive charge, the value of which proportionally increases with the concentration of adsorbed substances. For the material in question, i.e. the system of dispersed VO_2 in a PEG matrix with additives of QAS, one can expect the appearance of charges of op-

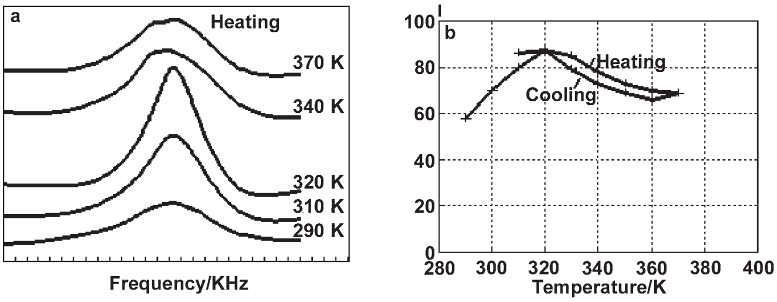

Fig. 4 Temperature-induced variations of the ^{1}H NMR spectra (a) and signal intensity (b) for a sample of VO_2 in a PEG matrix doped with QAS and containing 5 mass% of water

posite signs on the VO_2 particle surface. Actually, negatively charged ions of bromine are a more mobile type of ions. These ions can diffuse to the VO_2 surface, where they discharge to neutral atoms of Br. However, bromine atoms have a high reactivity. Therefore, they are likely to bind chemically with polymer molecules or with the VO_2 surface. In this case, near the surface one can observe the emergence of strong electric fields between negatively charged VO_2 particles and $(C_2H_5)_4N^+$ cations that are located within the polymeric matrix. Since the solubility of QAS in PEG is low, tetraethylammonium ions are located only near a small zone of the surface of VO_2 particles, which accounts for simultaneous existence of the semiconductive and metallic phases of VO_2 in a wide temperature region (340–365 K). It should be noted that in this temperature interval the width of the second signal is considerably smaller than that of the first one. So far as the signal width in the ^{1}H NMR spectra increases with the increasing concentrations of free electrons, the smaller width of the signal of polyethylene glycol molecules adsorbed on the VO_2 surface may be attributed to dielectrization of the VO_2 surface zones responsible for the appearance of this signal.

Furthermore, the following particularities of the temperature behavior of the sample are also worth noting:

1. The temperature of MSPT for the main portion of VO_2 is in the interval $330<T<340$ K, i.e. it is in agreement with the temperature of PT for dispersed VO_2 in a PEG matrix (Fig. 1), but the narrow signal can be detected in the spectra beginning with the temperature $T=320$ K.

2. Although with increasing temperatures the signal intensity decreases, the signal itself does not vanish upon heating of the sample up to the temperature $T=390$ K.

3. Under cooling of the sample the main portion of VO_2 passes into the semiconductive phase at a temperature of $330>T>320$ K, but the narrow signal in the spectra is observed even at the temperature $T=305$ K.

The phase heterogeneity of dispersed VO_2 in a PEG matrix decreases sharply, when PEG absorbs a small amount of water. Thus, absorption of 5 mass% of water by the polymeric matrix leads to the practically complete disappearance of the narrow signal component (Fig. 4). Besides, the effect of ‘memory’ also vanishes from the temperature dependence of the signal intensity $I=f(T)$ (Fig. 4b). Such a behavior of the system is evidently caused by an increase in the mobility of QAS cations in the polymeric matrix containing water. Moreover, under the action of the strong electric field that exists between the QAS cations and negatively charged surface of VO_2 particles these cations move towards the surface. The local electric field is confined within the gap between the QAS cations and VO_2 particle surface, and in terms of its geometry it is analogous to an electric field between a point charge and conducting surface.

The motion of the cations towards the surface leads to a decrease in the VO_2 particle surface area subjected to the action of the local electric fields. In addition, a chemical interaction of the QAS cations with the VO_2 surface is also possible, as a result of which the positive charge on nitrogen atoms of QAS disappears.

Conclusions

On the basis of the results of this study it is possible to conclude that small concentrations of QAS in a PEG matrix can exert a strong effect on the electronic structure of dispersed VO_2 particles. This is accompanied by the appearance of phase heterogeneity of VO_2, which manifests itself in the fact that with the onset of MSPT with increasing temperature one portion of the substance passes to the metallic state, and the other remains in the semiconductive state. The heterogeneity of a sample is observed in the wide temperature interval $305<T<390$ K. One of the probable causes of the observed phenomenon is a strong bonding of QAS cations with the polymeric matrix, while bromine anions diffuse to the VO_2 surface and discharge on it in the process of chemisorption. As a result, an electric field sets up, and the field lines are directed from cations localized in the polymer matrix to the VO_2 particle surface. The heterogeneity induced in the sample leads to the effect of ‘memory’ of its temperature history.

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