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Abstract

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APPLICATION OF THE ELECTRON PARAMAGNETIC RESONANCE METHOD TO THE STUDY OF ELECTRICAL-CONDUCTION MECHANISMS IN GLASSES OF THE TERNARY SYSTEM

$V_2O_5-P_2O_5-WO_3$

(Presented by Academician L. A. Artsimovich on 30 January 1967)

Recently the method of electron paramagnetic resonance (EPR) has found wide application in the study of the conduction mechanisms of crystalline and semiconducting compounds based on transition-metal oxides, since this method makes it possible to carry out a quantitative comparison of the contents of different valence forms of transition elements, which in turn can serve as a key to understanding the processes of electrical conductivity in these compounds.

In the present work the method was applied to the study of glasses of the ternary system $V_2O_5-P_2O_5-WO_3$. Investigation of this system is of interest because two of its components (V_2O_5 and WO_3) are the most active carriers of semiconducting properties in phosphate glasses. In addition, the electrophysical properties of glasses of this system must be quite distinctive, since the vanadium-phosphate component of them, at an P_2O_5 content above 35%, has p -type conductivity, whereas the tungsten-phosphate component always has n -type conductivity. The combination in one glass of components responsible for different types of conductivity seemed to us to exclude the possibility of an additive superposition of their electrophysical properties, which was to be verified in the present experiments.

According to existing ideas, the conductivity of vanadium-phosphate glasses is determined by electron exchange between two valence forms of vanadium (V^{4+} and V^{5+}), and that of tungsten-phosphate glasses by electron exchange between W^{5+} and W^{6+} . The ions V^{5+} and W^{6+} are diamagnetic, whereas the possibility of detecting V^{4+} and W^{5+} ions by the EPR method in glasses has been established earlier (¹⁻³). In the present work the EPR of glasses was investigated

whose compositions cover practically the entire glass-forming region of the system $V_2O_5-P_2O_5-WO_3$ (the interval of composition variation is 5-10 cat. %, and in the region of low VO_x content, 1 cat. %). Measurements were carried out on a standard RE 1301 radiospectrometer at room and liquid-nitrogen temperatures. The concentrations of paramagnetic centers were determined by double graphical integration of the first derivative of the EPR absorption curve. Weighed portions of $CuSO_4 \cdot 5H_2O$ single crystals were used as the standard sample. In parallel, measurements were made of the electrical conductivity of the glasses in the temperature interval from 20 to 400°, of the static magnetic susceptibility in the same temperature interval,* and also of the thermoelectric-power coefficient at 100 and 150°. The results of the experiments are presented in Figs. 1 and 2 and in Table 1.

* The measurements were performed at the Department of Magnetism of Moscow University by the inhomogeneous magnetic-field method.

Discussion of the Results

1. The EPR spectra for glasses of the binary system $V_2O_5-P_2O_5$ in the range of $PO_{2.5}$ content from 10 to 60 mol. % consist of a single broad isotropic line with $g = 1.96 \pm 0.01$ (see Fig. 1e) and may be assigned to the V^{4+} ion in an octahedral ligand field with an axial component (1, 3). The line width is practically constant on going from the observation temperature of room temperature to liquid-nitrogen temperature, while the intensity changes in accordance with the change in the Boltzmann distribution of populations of the energy levels. As follows from Fig. 2, the width and intensity of the line depend strongly on the composition of the glass. Curve 5, expressing the percentage content of V^{4+} ions (in mol. %), was calculated from static magnetic-susceptibility measurements. From a comparison of these curves it follows that the monotonic increase in the concentration of V^{4+} with increasing P_2O_5 content, established from magnetic-susceptibility measurements, corresponds to a sharp decrease in the intensity of the EPR signal in the region of $PO_{2.5}$ contents of 20-40%, i.e., the integral intensity of the EPR signals cannot serve as a characteristic of the V^{4+} content. Apparently, the amount of V^{4+} is so large that these ions combine into groups bound by exchange forces, within which rapid relaxation processes act, limiting the possibility of observing the signal from ions entering into these groups. The observed EPR line is due to "isolated" V^{4+} ions that are not part of such groups. In Fig. 2 attention is also drawn to the fact that in the concentration region $PO_{2.5} > 35\%$ there is a change in the sign of the thermoelectric-power coefficient α , indicating a change in the sign of the majority current carriers. With increasing $PO_{2.5}$ content, a monotonic increase in resistance is observed, with a small jump at a concentration of $PO_{2.5} \sim 35\%$.

Fig. 1. EPR spectra at 77°K in glasses of the ternary system $V_2O_5-P_2O_5-WO_3$ at constant concentration $PO_{2.5}$ (50 mol. %):

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

- a* —WO₃ 50%;
- b* —VO_x 1%, WO₃ 49%;
- c* —VO_x 5%, WO₃ 45%;
- d* —VO_x 10%, WO₃ 40%;
- e* —VO_x 30%, WO₃ 20%;
- f* —VO_x 50%.

Fig. 2. Dependence of the resistance $\lg \rho$ (1), the thermoelectric-power coefficient α (2), the integral intensity I (3) and width δH (4) of the EPR line, and the percentage content of V⁴⁺ ions (5), on the concentration of PO_{2.5} (mol. %) in glasses of the binary system P₂O₅—V₂O₅.

All these results make it possible to give the following interpretation of the conduction mechanism of vanadium phosphate glasses: at high concentrations of V₂O₅ (> 65%), when vanadium is present mainly in the pentavalent state and some part of it in the tetravalent state, conduction occurs by a “relay” charge transfer as a result of electron exchange between V⁴⁺ and V⁵⁺. At the same time, along with the motion of an electron through the matrix consisting of V⁵⁺ ions, there is motion of a “hole,” which is a valence-unsaturated V⁵⁺ ion and arises as a result of donation of an electron to a valence-saturated V⁴⁺ ion. The electronic character of the conductivity in this range of compositions is apparently due to the greater mobility of electrons as compared with holes. With a decrease in the V₂O₅ content (< 65%), the amount of V⁴⁺ begins to considerably exceed that of V⁵⁺, which leads to a decrease in the mobility of electrons and to the predominance of hole conductivity over electronic conductivity.

Table 1

Electrical parameters of certain glasses of the system V₂O₅—P₂O₅—WO₃

Composition no.	Composition (cat. %)	Composition (cat. %)	Composition (cat. %)	$\lg \rho$	Thermo- e.m.f., mV · deg ⁻¹
	W	V	P		
1	60	—	40	6.5	—350
2	50	—	50	5.4	—175
3	40	—	60	5.0	—125
4	30	—	70	5.4	—10
5	45	5	50	9.5	—250
6	40	10	50	9.8	+40
7	30	20	50	9.8	+150
8	20	30	50	9.8	+250
9	10	40	50	9.8	+250

Composition no.	Composition (cat. %)	Composition (cat. %)	Composition (cat. %)	$\lg \rho$	Thermo- e.m.f., $\text{mV} \cdot \text{deg}^{-1}$
10	—	50	50	9.35	+250

- The EPR spectrum of tungsten phosphate glasses with a WO_3 content from 20 to 60 cat.% consists of a single broad asymmetric line with $g = 1.68 \pm 0.02$ (Fig. 1a) and may be attributed to the W^{5+} ion (2). The magnetic susceptibility of tungsten phosphate glasses is very low, which indicates a small concentration of W^{5+} ions. It may therefore be assumed that the integral intensity of the EPR lines is proportional to the W^{5+} content. The monotonic increase in the intensity of the EPR lines with increasing $\text{PO}_{2.5}$ content thus indicates an increase in the concentration of W^{5+} , as should also be expected from the oxidation-reduction potentials of this medium. Assuming proportionality between the integral intensity of the EPR lines and the concentration of W^{5+} , the latter can be estimated: for composition no. 3 (Table 1) it has a value of $\sim 10^{18} \text{ cm}^{-3}$, which corresponds to an effective electron mobility $\mu = \sim 10^{-4} \text{ V} \cdot \text{cm} \cdot \text{sec}^{-1}$. Data on the resistance and thermo-e.m.f. for tungsten phosphate glasses are given in Table 1 (compositions nos. 1-4).

The character of the change in the thermo-e.m.f. coefficient and in the W^{5+} content as a function of glass composition makes it possible to suppose that the electrical conductivity of glasses in the $\text{WO}_3\text{—P}_2\text{O}_5$ system is associated with electron exchange between W^{5+} and W^{6+} . The extreme course of the resistance as a function of $\text{PO}_{2.5}$ content is explained by the opposite influence of two factors: a decrease in the total WO_3 content, leading to an increase in resistance, and an increase in the W^{5+} concentration, leading to a decrease in resistance.

- Thus, it has been established that: (a) in tungsten phosphate glasses, n -type conductivity is realized by electron exchange between W^{5+} and W^{6+} ; (b) in vanadium phosphate glasses with a high $\text{PO}_{2.5}$ content ($> 35\%$), hole conductivity is caused by the higher mobility of holes in a medium consisting mainly of V^{4+} ions and a small fraction of V^{5+} ions. It is therefore of interest to consider the electrical-conduction processes of the ternary system $\text{V}_2\text{O}_5\text{—P}_2\text{O}_5\text{—WO}_3$ along sections with a high $\text{PO}_{2.5}$ content. We studied three sections: $\text{PO}_{2.5}$ 40, 50, and 60 cat.%. The results are generally analogous; Table 1 and Fig. 1 present data for the section $\text{PO}_{2.5}$ 50 cat.%.

The resistance of glasses of the binary system $\text{WO}_3\text{—PO}_{2.5}$, upon addition of a third component, $\text{V}_{2.5}$, even in small amounts, increases sharply (on going from composition No. 2 to composition No. 5 by approximately 4 orders of magnitude), remains practically constant upon further replacement of W by V, and decreases somewhat on transition to the binary system $\text{V}_2\text{O}_5\text{—P}_2\text{O}_5$. Also

characteristic is the change in sign of the thermoelectric-power coefficient from negative to positive upon introducing $\text{VO}_{2.5} > 5\%$. It follows from Fig. 1 that, when $\text{VO}_{2.5}$ is added to tungsten phosphate glasses in an amount $\leq 2\%$, the EPR spectrum is determined by W^{5+} ions. With a further increase in the $\text{VO}_{2.5}$ content, the spectrum due to W^{5+} disappears and the characteristic hyperfine structure (h.f.s.) of V^{4+} appears (3). The increase in the intensity of this spectrum and the deterioration of the h.f.s. resolution at $\text{VO}_x > 10\%$ indicate an increase in the V^{4+} content as the total amount of V_2O_5 increases. At 20% VO_x there is complete disappearance of the h.f.s. as a result of overlap of the h.f.s. components broadened owing to dipole-dipole interaction. In the region of 30—40% $\text{VO}_{2.5}$, very weak and extremely broad lines are observed (~ 1300 Oe); this effect is associated with the formation of close groups of V^{4+} , arising at very high concentrations of V^{4+} . This conclusion is also confirmed by data on the static magnetic susceptibility.

Thus, the EPR spectra made it possible to establish that in glasses of the ternary system, only in a very narrow range of compositions adjoining the binary system $\text{WO}_3\text{—PO}_{2.5}$ (1—3 at.%), the electrical conductivity is determined by electron exchange between W^{5+} and W^{6+} . The sharp decrease in conductivity with a further increase in the V_2O_5 content is associated not with a decrease in electron mobility due to dilution of the conducting matrix (the tungsten matrix), but with a sharp reduction in the concentration of W^{5+} , apparently as a result of the reaction $\text{W}^{5+} + \text{V}^{5+} \rightarrow \text{W}^{6+} + \text{V}^{4+}$. Further increase in the $\text{VO}_{2.5}$ content leads to complete disappearance of W^{5+} ions and suppression of the tungsten phosphate component of the conductivity. The increase in vanadium content is accompanied by the appearance of conductivity characteristic of vanadium phosphate glasses with a high concentration of V^{4+} (p -type).

Conclusions

1. EPR spectra, in combination with measurements of static magnetic susceptibility, electrical conductivity, and thermoelectric-power coefficients, confirm that in glasses containing tungsten and vanadium oxides, conductivity is effected through mechanisms of the Fervé mechanism type.
2. The EPR spectra made it possible to estimate the concentration of W^{5+} and the effective mobility of electrons in tungsten phosphate glasses.
3. It has been established that, in the case of vanadium phosphate glasses, EPR spectra cannot serve as a characteristic of the V^{4+} ion content, owing to their high concentration in the range of compositions that has practically important values for electrical conductivity. Thus, a significantly greater mobility of the principal current carriers in tungsten phosphate glass has been found in comparison with vanadium phosphate glass.
4. From the EPR spectra it proved possible to trace the features of the mechanisms of electrical conductivity in different composition regions of glasses of the ternary system $\text{V}_2\text{O}_5\text{—P}_2\text{O}_5\text{—WO}_3$. In particular, a sharp

decrease in the concentration of W^{5+} ions upon the addition of small amounts of vanadium pentoxide to tungsten phosphate glasses has been established.

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