VANADATE SEMICONDUCTING GLASSES DOPED WITH OXIDES OF OTHER TRANSITION METALS
L. Bogomolova, V. Jachkin, M. Glassova, S. Spasibkina

To cite this version:
L. Bogomolova, V. Jachkin, M. Glassova, S. Spasibkina. VANADATE SEMICONDUCTING GLASSES DOPED WITH OXIDES OF OTHER TRANSITION METALS. Journal de Physique Colloques, 1981, 42 (C4), pp.C4-993-C4-996. <10.1051/jphyscol:19814216>. <jpa-00220845>

HAL Id: jpa-00220845
https://hal.archives-ouvertes.fr/jpa-00220845
Submitted on 1 Jan 1981

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
VANADATE SEMICONDUCTING GLASSES DOPED WITH OXIDES OF OTHER TRANSITION METALS

L.D. Bogomolova, V.A. Jachkin, M.P. Glassova and S.N. Spasibkina
Institute of Nuclear Physics, Moscow State University, Moscow 117234, USSR

Abstract.- The EPR spectra, electrical conductivity and activation energy have been measured in barium-vanadate glasses doped with CuO, Mn₂O₃, Fe₂O₃, Co₂O₃ and Cr₂O₃ impurities in concentration from 0.1 to 7 wt.%. The results are interpreted in terms of distinct interactions between vanadium and impurity ions.

Introduction.- The EPR study of barium-vanadate glasses with CuO impurity has shown (1) that Cu²⁺ and V⁴⁺ ions form the mixed exchange pairs. The single EPR line with g=2.08 has been attributed to these pairs coupled by strong ferromagnetic interaction. The formation of mixed pairs leads to the increase in total carrier concentration by the impurity electrons belonging to the pairs and to the change in the activation energy and effective mobility. The aim of the present work is the study of the valence states of the impurity transition metals (Mn, Fe, Co, Cr) in barium-vanadate glasses, their interactions with vanadium ions and effects on the electrical conductivity of these glasses.

Experimental.- The glasses with the base composition 35 mol.% BaO and 65 mol.% V₂O₅ (denoted by BV) were prepared. Four series of glasses BV doped with different impurities of transition metal oxides (M₂O₃) were investigated. These were glasses BV contained from 0.1 to 5 wt.% Mn₂O₃ (Series Mn-BV), glasses BV contained from 0.3 to 7 wt.% Fe₂O₃ (Series Fe-BV), glasses BV contained from 0.5 to 7 wt.% Co₂O₃ (Series Co-BV) and glasses BV contained from 1 to 5 wt.% Cr₂O₃ (Series Cr-BV). EPR measurements were carried out using X-band spectrometer RE-1306 from 77 to 470 K. The resistivity was measured over a temperature range from 60 C to a temperature near to the glass transition (~260-270 C) using a MOM-3 ohmeter.

Results.- We show the EPR spectrum of the base glass BV in Fig.1a. This is due to V⁴⁺ ions and can be described by an axial spin Hamiltonian with parameters gₘₘ = 1.924 ± 0.004, gₘₛ = 1.960 ± 0.005, aₘₘ = (157 ± 2).10⁻⁴ cm⁻¹ and Aₛ = (54 ± 2).10⁻⁴ cm⁻¹. Fig.2 shows the parallel hyperfine structure (hfs) components of V⁴⁺ EPR spectrum for m=7/2 and m=5/2 in the glass BV and in the glasses of Mn-BV series containing 0.3 and 0.5 wt.% Mn₂O₃.
It is seen that the linewidths of the hfs components are greater in the Mn-BV glasses than in the BV glass, and they increase with increasing Mn$_2$O$_3$ content. The hfs components are less clearly observed in the samples with 1 or 2 wt.% Mn$_2$O$_3$ and after 2 wt.% Mn$_2$O$_3$ hyperfine structure of V$^{4+}$ disappears completely. Single broad symmetric line is observed in glasses containing from 3 to 5 wt.% Mn$_2$O$_3$ (Fig. 1b). The linewidth is almost constant in these samples (430 Oe) and $g$-value varies from 2.009 to 2.018. The increase in the integrated intensity of this line is proportional to Mn$_2$O$_3$ content. The width of the line in the sample containing 5 wt.% Mn$_2$O$_3$ decreases from 470 to 390 Oe when temperature increases from -150 to +200 C. No other lines were observed in the glasses of Mn-BV series.

In contrast to the Mn-BV series the $g$=4.3 line due to Fe$^{3+}$ ions is observed in all the glasses of Fe-BV series. This is asymmetric with peak-to-peak width about 150-160 Oe at 0.5-1 wt.% Fe$_2$O$_3$. This line was also observed in the samples with high Fe$_2$O$_3$ contents but its intensity and width cannot be measured because of an overlap with other line (Fig. 1c). In the glasses containing from 0.3 to 1 wt.% Fe$_2$O$_3$ the hfs EPR spectrum of V$^{4+}$ ions is observed clearly. The wid-
Fig. 2: temperature dependence of the integrated intensity of EPR spectra

The hfs components increase with increasing Fe$_2$O$_3$ content, and the broad single line with g$^2$ is observed after 2 wt.% Fe$_2$O$_3$. These results are similar to those for Mn-BV glasses. However, the width of the g$^2$ line is greater in Fe-BV glasses than in Mn-BV glasses (Fig. 1) and this increases with Fe$_2$O$_3$ concentration.

The hfs EPR spectrum due to V$^{4+}$ ions is only observed in the glasses of the Co-BV series at room temperature. The temperature dependence of the intensity of this EPR spectrum in the glass containing 7 wt.% Co$_2$O$_3$ is shown in Fig. 3. New very broad line appears in a low magnetic field at 77 K in all the samples of series Co-BV (Fig. 1).

The hfs EPR spectrum due to V$^{4+}$ is observed in the glasses of the Cr-BV series in the temperature range from 77 to 300 K. The widths of hfs components are constant for Cr$_2$O$_3$ content ranging from 1 to 5 wt %. However, the widths of hfs components and integrated intensity of the spectrum increases suddenly when temperature increases to 35 C in all the samples of this series (Fig. 3).

The dependence of the resistivity at 60 C on M$_2$O$_3$ concentration in barium vanadate glasses is shown in Fig. 4. It can be seen that this increases with increasing M$_2$O$_3$ content in all the series. In the binary glass BV the resistivity at 60 C is 6.10$^6$ ohm cm. The temperature dependence of the resistivity for this glass can be represented by two straight lines with differing slopes, that is, with two different activation energies. The activation energy $E_a = 0.382$ eV from 60 to 200 C and $E_a = 0.15$ eV at higher temperature. This result is quite similar to that reported in (2). In almost all the glasses containing M$_2$O$_3$ the temperature dependence of the resistivity can be roughly represented by a single straight line with an activation energy increasing to 0.42-0.47 eV at 5-7 wt.% M$_2$O$_3$.

Discussion.- The analysis of EPR spectra of barium-vanadate glasses containing impurities of five different transition metal oxides show the considerable interactions between them and vanadium ions. It is
essential that these interactions are different depending on an impurity. Some similar features can be found only for Fe$_2$O$_3$ and Mn$_2$O$_3$ impurities. Both oxides lead to broadening of hfs components of the V$^{4+}$ spectrum in the samples with low contents of Fe$_2$O$_3$ and Mn$_2$O$_3$.

Such behavior can be interpreted in terms of dipole-dipole interactions between vanadium (4+) ions and Fe or Mn ions. However, if the g=4.3 line indicates the presence of Fe$^{3+}$ ions in the Fe-containing glasses, the valence states of Mn in the Mn-containing glasses are not known. The concentration dependence of the integrated intensity of EPR spectrum in Mn-BV glasses indicate the presence of Kramers' manganese ions (Mn$^{2+}$, Mn$^{4+}$, Mn$^{6+}$) in the glass BV containing 5 wt.% Mn$_2$O$_3$.

The single line with g=2.018 was observed. It is known that for ferromagnetic coupling of two dissimilar ions $S_1$ and $S_2$ the pair g-value is intermediate between those for the single-ions. On the contrary in the antiferromagnetic state there is an enhancement of the effectiveness of the ion with higher spin, and a contribution with reversed sign from the other ion. This fact allows the pair g-values to lie outside the range of the single-ion values. It was shown that the effective g-value for pairs of ions of different spins ($S_1 > S_2$) in the case of antiferromagnetic coupling (5) is

$$g = \left( \frac{S_1 + 1}{S_1} \right) g^1 - \left( \frac{S_2}{S_2} \right) g^2 \left( S_1 - S_2 + 1 \right)$$

(1)

It is easily seen that effective g=2.018 for Mn$^{2+}$-V$^{4+}$ pair can be obtained only for $g^1 > 2$, and $S_1 = 5/2$. Therefore, we assume that the line with g=2.018 is due to antiferromagnetically coupled pairs Mn$^{2+}$-V$^{4+}$ ($g^1$, $S_1$ and $g^2$, $S_2$ refer to Mn$^{2+}$ and V$^{4+}$ respectively.

It is well known that Co$^{2+}$ ions are fast relaxing in oxide glasses and their EPR lines are too broad to be observed at temperatures as high as 300 or 77 K. The EPR spectrum of Co(2+) in oxide glasses has been detected only at 4.2 K (4). It consists of a single broad asymmetric line with $g=2.4$. We assume that the majority of Co ions is in the Co$^{3+}$ state in the glasses of Co-BV series. Then the decrease in the EPR signal of the V(4+) ions can be explained by electron transfer from V$^{4+}$ to Co$^{3+}$ in the mixed pair V$^{4+}$ - O - Co$^{3+}$. The temperature dependence of the integrated intensity of EPR spectrum of V$^{4+}$ ions was used to estimate the magnitude of exchange energy for this pair [2J $\approx$ 130 cm$^{-1}$]. The line in low magnetic fields which appears at 77 K in glasses of Co-BV series is possibly due to Co$^{2+}$ ions.

The sudden change in the EPR spectrum of V$^{4+}$ ions at 35 C in the glasses of Cr-BV series can be presumably attributed to phase transition. This transition probably occurs in the vitreous phase since the shape of the spectrum and its hfs linewidths are characteristic of V(4+) in glasses.

References.