JOURNAL OF MATERIALS SCIENCE 17 (1982) 3221–3226

ESR study of the equimolar $PbO-V_2O_5$ system

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The semiconducting system 50 mol % $PbO-V_2O_5$ has been studied by electron spin resonance (ESR) in the temperature range 150 to 675 K. Depending on the cooling rate, this system can be obtained from the melt as an amorphous phase, as polycrystalline lead-metavanadate (PbV_2O_6), or as two different mixtures containing polycrystalline and amorphous phases. In all these materials the ratio V^{4+}/V_{tot} has been measured by wet analysis showing that the V^{4+} concentration is nearly constant. It has been possible to show that the appearance of very different ESR line-shapes for the various materials is due to the difference in the hopping rate of the charge carriers. In particular the presence of a well-defined hyperfine structure is characteristic of the amorphous phase, in which the mobility of the charge carriers is lowered by the presence of a term W_D in the expression of the hopping rate. The lead-metavanadate ESR spectrum shows the presence of two lines of different widths; this fact has been explained assuming the presence of two distinct jumping rates. No temperature variation of the spectra has been observed at low temperatures. The high temperature spectra have permitted us to follow the thermal evolution of the system.

1. Introduction

It is well known that glasses containing high concentrations of vanadium pentoxide have semiconducting properties due to a hopping process of the unpaired 3d electron from a V^{4+} to a V^{5+} ion. The unpaired electrons induce a lattice polarization, and for this reason the charge carriers constituted by the extra electrons and the lattice deformation are called polarons.

The most studied systems by electron spin resonance (ESR) are $V_2O_5-P_2O_5$ in various compositions [1–5], amorphous V_2O_5 [6], barium borate glasses [7] and $V_2O_5-TeO_2$ [8].

We have undertaken the study of the equimolar $PbO-V_2O_5$ system which, depending on the thermal treatment, can be obtained either as a glass or in two different phase-separated systems. At high temperatures all these materials give rise to polycrystalline lead-metavanadate [9]. The obtained ESR spectra are greatly affected by thermal treatments. In the amorphous phase in fact the spectrum shows a well-resolved hyperfine structure, whereas in the phase-separated samples and in lead-metavanadate the ESR spectrum is entirely different.

The presence of such substantially different features in the ESR spectra of the V^{4+} ion in distinct conditions has been generally attributed to the difference in the concentration of the V(IV) species in the glasses which causes both dipolar broadening and exchange narrowing of the lines [1–4].

The electron paramagnetic resonance of $V_2O_5-P_2O_5$ glasses containing 10 to 50 mol % P_2O_5 have been studied by Nagiev [1]. In this work the disappearance of the hyperfine structure and the occurrence of two lines was explained in terms of a microphase separation. One of the phases is supposed to be richer in P_2O_5 and should have a higher V^{4+}/V_{tot} ratio, so giving the broad reson-

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ance line, whereas the other, richer in V_2O_5 and having a lower V^{4+}/V_{tot} ratio, should give the narrow line. More recently, glasses with different V_2O_5 contents have been studied [2–4], but only in one case [5] has the hopping rate of the conducting polarons been considered as a factor which might determine the shape of the lines. The present study of the equimolar V_2O_5–PbO system has shown that it is possible to explain the variations of the spectra following the latter scheme. In particular it will be shown that at least the qualitative features of the ESR lines are strictly linked to the mobility of the polarons in the samples.

2. Preparation and characterization of the samples

Equimolar amounts of PbO and V_2O_5 (Carlo Erba reagent grade) were melted in an electric oven at 800° C under normal atmosphere. The melts were quenched on materials having different thermal conductivities, i.e., stainless steel, copper and graphite. To obtain the very fast cooling rate graphite was used, previously cooled with liquid nitrogen. The samples obtained at different cooling rates were characterized by X-ray powder diffraction, scanning electron microscopy (SEM), EDS microanalysis and differential thermal analysis (DTA). They can be divided in the four sets of Table I [9]. The V^{4+}/V_{tot} ratio was determined by wet chemical analysis methods [10], and showed very small variations for the four sets.

3. ESR spectra description

The ESR spectra were obtained on a Bruker Spectrospin ER 200 D Spectrometer utilizing a TE_{102} rectangular cavity. A field modulation of 100 kHz was used. Variable temperature measurements were made by boiling off liquid nitrogen and passing the cold gas through a regulating heater and a flow Dewar which was inserted into the cavity. In this way it was possible to vary the temperature between − 150 and 0° C. The high temperature measurements were performed by blowing hot air through the flow Dewar. A maximum temperature on the samples of 400° C was obtained in this way. Representative ESR spectra of each set of the previously described samples are shown in Figs 1 to 3. There is no doubt that the amorphous phase spectrum and some of the features of the X material spectrum can be fitted by the Hamiltonian [11, 12]

$$H = g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp}(S_x I_x + S_y I_y),$$

where the symbols have the usual meaning.

The experimentally determined spin Hamiltonian parameters are listed in Table II. For the samples for which no hyperfine structure has been observed the effective g value (g_e) is given together with the line-width.

The spectra shown in Figs 1 to 3 were previously observed in vanadium-containing glasses [1–13] and particularly in vanadium phosphate glasses which are by far the most studied [1–5]. As pointed out before the variations in the ESR line-shape have been previously explained on the basis of different V^{4+} concentrations. In the present case the almost constant value of the V^{4+}/V_{tot} ratio seems to rule out the possibility that the variations in the line-shape could be attributed to differences in the V^{4+} concentration. Moreover in the case of the amorphous phase and in that of lead-metavanadate for which phase segregation has been ruled out by electron microscopy [9] it is impossible to suppose the existence of local fluctuations of the V^{4+}/V_{tot} ratio which would produce two different ESR lines. It is interesting to note that the shape of the metavanadate spectrum is very similar to that of

TABLE I Characteristics of the samples

Set of samples	Phases	Crystalline compound	V^{4+}/V_{tot}	Cooling rate
Amorphous	Amorphous	None	0.0170	Very fast
X material*	Amorphous and Polycryst.	α-$Pb_2V_2O_7$†	0.0176	Fast
Y material*	Amorphous and Polycryst.	β-$Pb_2V_2O_7$†	0.0216	Slow
Lead-metavanadate	Polycryst.	PbV_2O_6	0.0160	Very slow

*X material and Y material are conventional names.

†α-$Pb_2V_2O_7$ and β-$Pb_2V_2O_7$ are allotropic, metastable phases of chervetite, which is the only known stable form of $Pb_2V_2O_7$.

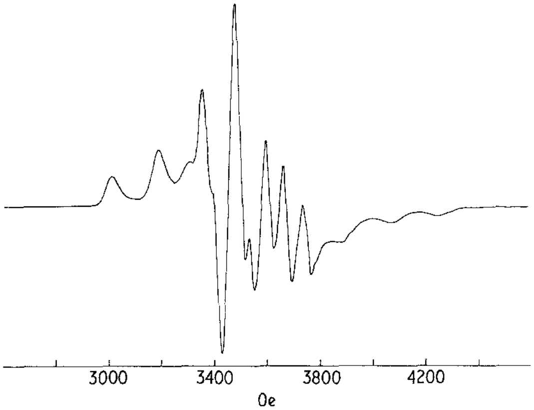

Figure 1 Room temperature ESR spectrum of the amorphous phase.

the samples of composition 54:46 mol % V_2O_5–P_2O_5 and 50:50 mol % V_2O_5–P_2O_5 studied by Nagiev.

Only in the case of X and Y materials for which phase separation has been observed can the variation of the line-shape be attributed to a fluctuation of the local concentration of the V(IV) species. It should be remembered that the concentration of the V(IV) ions does not necessarily follow that of the total vanadium species. In this case it also seems to be difficult to explain the observed variations in the line-shapes in terms of fluctuations of the local concentration of the V(IV) species.

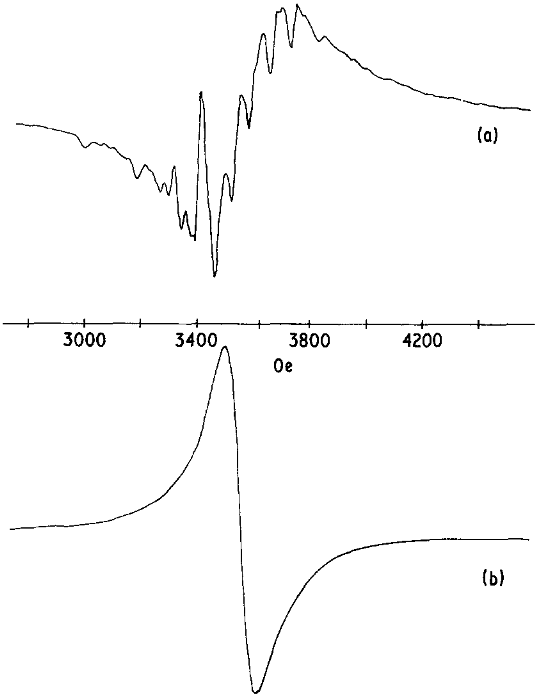

Figure 2 Room temperature ESR spectrum of (a) the X material and (b) the Y material.

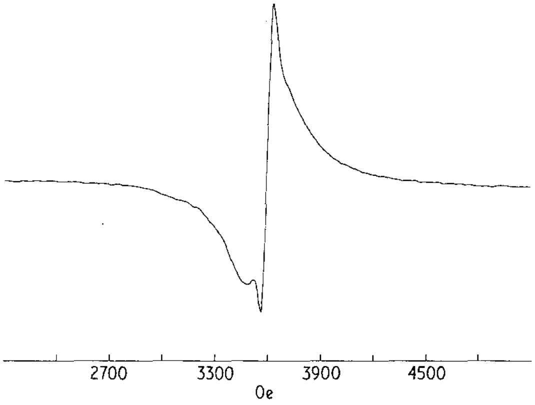

Figure 3 Room temperature ESR spectrum of the polycrystalline lead-metavanadate.

4. Discussion of the ESR species

4.1. Amorphous phase

The spin Hamiltonian parameters obtained from the amorphous phase spectra resemble very closely those characteristic of the vanadyl ion (VO^{2+}) in many organic and inorganic compounds. It can be assumed that the tetravalent vanadium ions occupy tetragonally distorted octahedral sites. This fact agrees with the local environment of vanadium as determined by X-ray diffractometry in PbV_2O_6 [14] which is shown in Fig. 4.

Translationally equivalent octahedra share corner oxygen atoms and extend infinitely along the **b**-axis. The lead atoms share oxygen atoms with three of these chains. As it is apparent from the figure there are two sets of translationally different vanadium ions in the PbV_2O_6 structure.

There is no evidence in the ESR spectrum of the amorphous phase of two different sets of the spin Hamiltonian parameters. It should be noticed that the differences in the bond lengths in PbV_2O_6 are not very large [14] and that in passing from a crystalline to an amorphous phase these values can be modified. The most striking feature of the spectrum is certainly the presence of a well resolved hyperfine structure which is completely absent in the crystalline phase at the same V^{4+} concentration. This fact can be explained by taking into account that in glasses the jumping frequency of the charge carriers is proportional to $\exp(-W/kT)$ where $W = \frac{1}{2}W_D + W_H$ [15–16]; the term W_D is the mean energy difference between adjacent vanadium sites due to the disordered nature of

TABLE II ESR experimental parameters

Set of samples	$g_{\parallel}$	$g_{\perp}$	g_e	$A_{\parallel}$ (10^{-4} cm^{-1})	$A_{\perp}$ (10^{-4} cm^{-1})	ΔH(Oe)
Amorphous	1.911 ± 0.002	1.963 ± 0.002		164 ± 1	52 ± 1	
X material	1.893 ± 0.002	1.962 ± 0.002		175 ± 1	56 ± 1	
X material central line			1.94 ± 0.05			350
Y material			1.951 ± 0.002			123
Lead-metavanadate			1.932 ± 0.002			177 72

the glass and W_H is the activation energy for the hopping process of the polarons between two identical sites.

In the case of amorphous samples it is possible to suppose that the leading term is W_D, and that the jumping rate of the polaron is low. This fact, together with the relative low concentration of the paramagnetic species ($V^{4+}/V_{tot} = 0.017$) allows the observation of the hyperfine structure. The jumping frequency of polarons depends on temperature and for this reason also the shape of the ESR spectra should be temperature dependent. The lack of this dependence between 150 and 300 K requires some comment.

For each possible temperature the electrons' energy will be spread by an amount of the order of kT; at low temperature only those sites which correspond to the lower energy will be occupied. If $W_D \gg kT$ (for $T = 300$ K) the distribution among different sites at various temperatures is irrelevant and the ESR line is independent of temperature. Though there is no way of determining the value of W_D from the ESR spectra, it seems reasonable to assume that this value should be higher than that of W_H as determined in the case of vanadium phosphate glasses [15], i.e., $W_D \approx 0.45$ eV.

The result of this fact is that the high W_D value "freezes" the hopping process, thus permitting the observation of the well-resolved hyperfine structure characteristic of the amorphous phase.

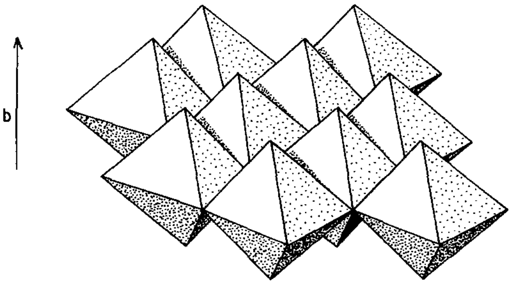

Figure 4 Edge-shared VO_6 chains in PbV_2O_6. There are two sets of translationally equivalent octahedra. The lengths of the V–O bonds are different for the two sets.

4.2. Lead-metavanadate spectra

The ESR spectra of polycrystalline lead-metavanadate show two lines of different width, but within the experimental error, at the same value of g_e. Both lines are strongly narrowed by exchange. The hopping process between adjacent sites, responsible of the narrowing, can be described following Mott in the way shown in Fig. 5a. The activation energy for the hopping process W_H is $W_H = \frac{1}{2}E_p$ where E_p is the polaron binding energy. It must be noticed that this scheme holds as long as the two adjacent sites are identical.

It is natural to ask whether the presence of two ESR lines can be explained in terms of two dif-

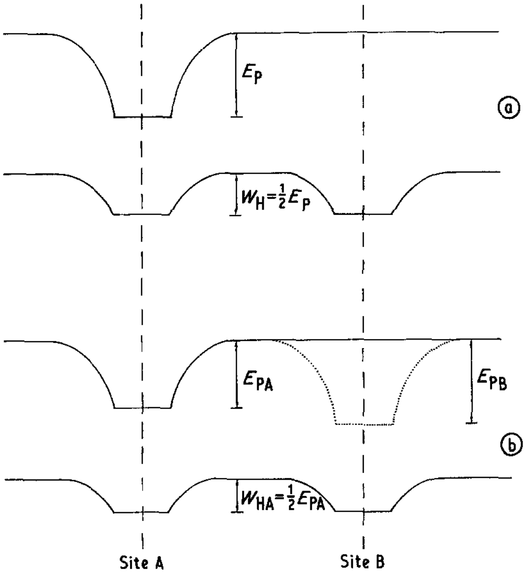

Figure 5 Schematic representation of the hopping of one electron between two equivalent sites (a) By associating two different energies with the polaron in the two sites (b) the activation energy of the hopping process depends on the energy of the starting level.

ferent sites. A very simple way of taking into account the presence of two nonidentical adjacent sites is that of associating two different potential wells to the polaron at the positions of the A and B sites. In this situation, which is sketched out in Fig. 5b, the potential energy of the polarization wells induced by lattice vibrations will differ by ΔE. For this reason there will be two different values of the activation energy, one W_{HA} for electrons leaving A sites and the other, W_{HB}, for electrons leaving B sites. The jumping frequency for electrons hopping from A sites will be proportional to $\exp(-W_{\mathrm{HA}})$, whereas that for electrons hopping from B sites will be proportional to $\exp(-W_{\mathrm{HB}})$. For electrons moving between different sites the jumping frequency will be that corresponding to the higher activation energy.

It is thus possible to assume that the presence of two different lines in the ESR spectrum of lead-metavanadate could be explained in terms of two different jumping rates. Also, in the case of lead-metavanadate no temperature dependence of the ESR line has been observed. This fact can be explained by the hypothesis that $W_{\mathrm{H}} < kT$ (for $T = 150$ K).

4.3. Mixed materials

As has been previously seen, the two intermediate phases are characterized by the presence in the samples of an amorphous and a polycrystalline phase. The stoichiometry of the crystalline phases has been found to be different from that of lead-metavanadate, so the amorphous phase of these samples must also have a composition different from that of the original batch.

For the X material, for which the hyperfine structure is still evident, the Hamiltonian parameters are different from those found in the original amorphous phase. Moreover there is evidence for the presence of at least a second different set of parameters. No attempt has been made to evaluate these parameters because of the weakness and the overlapping of these lines. The broad central line seems to originate in the crystalline phase.

The Y material spectrum consists of a single line with no trace of hyperfine structure. An attempt to analyze the line-shape of this line by the method of moments [17] has shown that the line is nearly, but not exactly, Lorentzian. The fact that the metavanadate spectrum is the sum of two different lines justifies the hypothesis that in this case the deparature from the Lorentzian line-shape could also be explained by the presence of more than one line of different width within the observed spectrum.

5. High temperature ESR spectra

By running the ESR spectra at high temperature it was possible to follow the evolution which takes place in the glass and which precedes the formation of the lead-metavanadate. The spectra show that the hyperfine structure characteristic of the amorphous phase is present up to a temperature of 380° C. At this temperature there is evidence of the appearance of the lead-metavanadate spectrum. This phase transformation is proved by the spectra to be irreversible.

6. Conclusions

The ESR study of the various phases and mixtures in which it is possible to obtain the equimolar $\mathrm{PbO{-}V_2O_5}$ system has shown that the jumping rate of the charge carriers is the factor which most affects the shape of the ESR lines. In particular it seems that the presence of the hyperfine structure is characteristic of the amorphous phase because of the presence in this case of a large term $W_{\mathrm{D}} \gg kT$ ($T \simeq 300$ K) in the relationship which gives the jumping rate of the charge carriers. The presence of two different lines of distinct line-widths observed in the case of the lead-metavanadate can be explained by assuming the presence of two different jumping rates of the charge carriers. The X and Y materials spectra, and probably most of the spectra found in literature [1–5], seem to stay between these two extremes. They are in fact composed of a crystalline phase plus an amorphous phase. A different jumping rate corresponds to each phase and hence a different ESR spectrum. The resulting spectrum is the overlap of these contributions.

Acknowledgements

The authors are grateful to Mr R. Zonta for assistance during the preparation of the work. This work was financially supported by CNR (Italian National Research Council) in the Progetto Finalizzato per la Chimica Fine e Secondaria.

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Received 24 February
and accepted 1 April 1982