

EPR AND MAGNETIC INVESTIGATIONS OF CHROMIUM IONS IN TeO₂ BASED GLASSES

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Electron paramagnetic resonance (EPR) and magnetic susceptibility measurements on $x\text{Cr}_2\text{O}_3 \cdot (100-x)[70\text{TeO}_2 \cdot 20\text{B}_2\text{O}_3 \cdot 5\text{MO}]$ glasses with $\text{MO} \Rightarrow \text{PbO}, \text{SrO}, \text{SrF}_2$ and $0 < x \leq 20\% \text{ mol}$ are performed. The EPR spectra due to the Cr^{3+} ions in vitreous matrix revealed the structural details of the diamagnetic host, the coordination and the distribution of these ions, the EPR parameters being sensitive to the local symmetry, the character of the chemical bonds as well as of the structural factors. EPR and magnetic susceptibility data have shown that the Cr^{3+} ions are present in the studied glasses as isolated species, coupled by dipol-dipol and/or negative superexchange interactions. The strength of these interactions was determined in function of x and different modifiers of vitreous matrix.

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1. Introduction

Structural and physical properties of tellurite [1] and boro-tellurite [2] glasses were intensely studied for their scientific interest and practical applications. Tellurite glasses have a scientific and technical interest because of their low melting temperature, high refractive index, high dielectric constant and good infrared transmission [3]. The TeO₂ forms stable semiconducting glasses in combination with B₂O₃, P₂O₅ or V₂O₅ [4]. The addition of other oxides in the TeO₂ matrix changes the coordination of the Te from a TeO₄ tetragonal bipyramid (TBP) group to a TeO₃ trigonal pyramid (TP) [5,6,7].

The local order in diamagnetic vitreous matrices may be revealed by the chromium ion, used as probes in EPR experiments. Data have been reported for a great variety of glasses such as phosphate [8], borate [9], bismuth-germanate [10] and boro-sulphate [11], where Cr^{3+} species were detected as isolated in strongly distorted octahedral symmetric sites subjected to strong ligand field effects, or associated in exchange coupled pairs, depending on the Cr₂O₃ content of glass. There also have been detected Cr^{5+} species in some oxide vitreous materials [12].

This paper presents our results obtained by means of EPR and magnetic susceptibility measurements on Cr containing 70TeO₂-25B₂O₃-5PbO, 70TeO₂-25B₂O₃-5SrF₂ and 70TeO₂-25B₂O₃-5SrO glasses and how EPR and magnetic susceptibility measurements data may reveal the microheterogenous structure of tellurite glasses.

2. Experimental

The investigated systems: (1) - $x\text{Cr}_2\text{O}_3 \cdot (1-x) [70\text{TeO}_2 \cdot 25\text{B}_2\text{O}_3 \cdot 5\text{PbO}]$, (2) - $x\text{Cr}_2\text{O}_3 \cdot (100-x)[70\text{TeO}_2 \cdot 25\text{B}_2\text{O}_3 \cdot 5\text{SrO}]$, (3) - $x\text{Cr}_2\text{O}_3 \cdot (100-x)[70\text{TeO}_2 \cdot 25\text{B}_2\text{O}_3 \cdot 5\text{SrF}_2]$ were obtained from starting materials Cr₂O₃, TeO₂, H₃BO₃ and PbO (1), SrCO₃ (2), respectively SrF₂ (3) of reagent grade purity. The temperatures and the melting conditions were the same: 1000 °C for 6 min.

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Sintered corundum crucibles were used and the quenching at room temperature was realized by pouring the molted material on a stainless-steel plate. The samples' structure was tested by means of X-ray diffraction, selecting the range of concentration for which the diffractogram did not reveal any crystalline phase. Typical glasses were obtained up to 20 mol% Cr_2O_3 for systems (1) and (3) and up to 10 mol% Cr_2O_3 for system (2).

The EPR measurements were performed at room temperature in X-band (9.4GHz) and 100 kHz field modulation with a JEOL-type equipment.

Magnetic susceptibility measurements were obtained from a Faraday-type balance, in the 80-300 K temperature range. The magnetic susceptibility values were determined by taking into account the measured data due to the diamagnetism of the glass matrix.

3. Results and discussion

3.1. EPR and magnetic susceptibility studies of glasses from system (1)

Fig. 1 shows EPR absorption spectra of the system (1) glasses due to Cr^{3+} ($3d^3$; $^4F_{3/2}$) ions. For all samples the spectrum consists of low-field absorption centered at $g \approx 4.8$ and high-field absorptions centered at $g \approx 1.97$, according to the theory [13].

According to Fig. 1 the low field absorption of Cr^{3+} ions in $70\text{TeO}_2 \cdot 25\text{B}_2\text{O}_3 \cdot 5\text{PbO}$ glasses does not depend on the Cr_2O_3 content of the sample. Neither the shape nor the intensity of the absorption line was affected within the experimental errors by the Cr_2O_3 content increasing, proving a great structural stability of the matrix when Cr^{3+} ions accumulate. The isolated ions preserve their ability of ordering their vicinity in structural units of a certain symmetry. This evolution of the matrix structure is not characteristic for the Cr^{3+} containing vitreous systems previously studied by us [4,14]. The structural units involving Cr^{3+} in sites of strong ligand field became less represented as the Cr_2O_3 content increases.

As shown in Fig. 1 the high field absorption at $g \approx 1.97$ increases with the Cr_2O_3 content of the sample within $1 \leq x \leq 20$ mol%. The high-field absorption, attributed to isolated Cr^{3+} ions in strongly distorted sites, increases in intensity when the Cr_2O_3 content of samples rise to 20 mol%. The site symmetry is predominantly rhombic with slightly different axial distortions of the Cr^{3+} ions vicinity. Consequently, the absorption line is broadened due to the superposition of absorptions: as background of the absorption at $g \approx 4.8$ is another broad absorption at $g \approx 4.0$ (approximated by the dotted line in Fig. 1) which may be attributed to sites with a predominantly axial character [15]. The low-field resonance at $g \approx 5.0$ detected for Cr^{3+} ions spectra in glasses is attributed to isolated Cr^{3+} ions in distorted sites due to strong ligand-field effects.

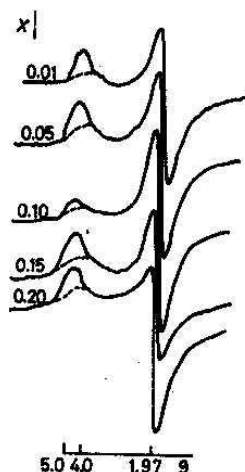


Fig. 1. EPR absorption spectra in system (1).

The line width, ΔH , of the $g \approx 1.97$ absorption, depends on sample composition is presented in Fig. 2. After an increase for $1 \leq x \leq 3$ mol% Cr₂O₃, the line width decreases abruptly within a short concentration range ($3 \leq x \leq 10$ mol% Cr₂O₃) and then increases again. There is a narrowing effect on the EPR absorption line for samples containing $x < 3$ mol% Cr₂O₃. These ions are involved only in dipole-dipole type interactions and magnetically isolated.

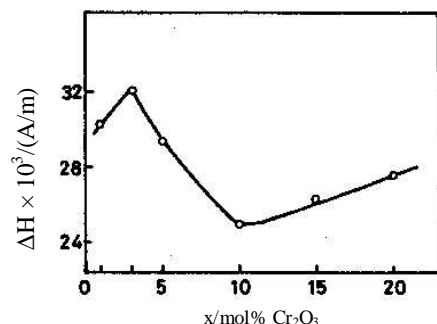


Fig. 2. Line-width dependence on the Cr₂O₃ content, for $g = 1.97$ absorption for system (1).

For $x > 3$ mol% the line-width increasing is stopped by narrowing mechanisms due to exchange-type interactions. These balance the dipolar broadening, both mechanisms simultaneously acting on the Cr³⁺ ions, which now are no more isolated but magnetically coupled. The exchange narrowing is efficient within $3 \leq x \leq 10$ mol%. For $x > 10$ mol% the magnetic interaction seems to be affected by structural disordering of the aggregates involving Cr³⁺ ions, and the line broadens again.

In contrast to Cr³⁺ in sites giving rise to the low-field absorptions, the local order around Cr³⁺ enhancing absorption at $g \approx 1.97$ is very sensitive to the progressive Cr³⁺ ions accumulation in the vitreous matrix.

The magnetic susceptibility data were obtained from the temperature dependence of the reciprocal magnetic susceptibility of the investigated glasses presented in Fig. 3. For glasses containing $x \leq 3$ mol% Cr₂O₃ this dependence obeys a Curie law, suggesting magnetically isolated Cr ions in this concentration range. For these compositions EPR detected electrically isolated Cr³⁺ ions, or ions subjected to dipole-dipole interactions. For compositions containing $x > 3$ mol% Cr₂O₃ the dependence in Fig. 3 obeys a Curie-Weiss law, with negative paramagnetic Curie temperature, θ_p . For these glasses, the high temperature susceptibility data indicate negative exchange interactions between Cr ions, which are predominantly antiferromagnetically [15] coupled.

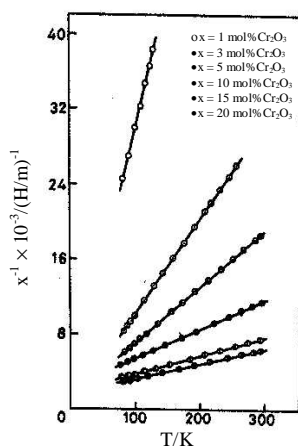


Fig. 3. Temperature dependence of the reciprocal magnetic susceptibility for system (1).

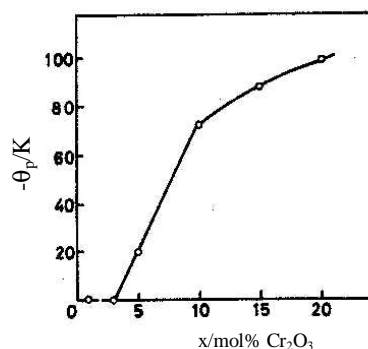


Fig. 4. Composition dependence of the θ_p for system (1).

The composition dependence of the paramagnetic Curie temperature, θ_p , is presented in Fig. 4. The absolute magnitude of θ_p linearly increases with $3 \leq x \leq 10$ mol% Cr_2O_3 . For $x > 10$ mol% Cr_2O_3 the slope of the increment becomes much slower, indicating weaker exchange coupling between Cr ions, in accord to literature [4,17]. This intensity loss of the exchange interaction occurs in more disordered glass structures. The molecular field constant values, $J = \theta/C_M$, calculated for the experimental data are plotted in Fig. 5. For $x \leq 3$ mol% Cr_2O_3 , one obtains $J = 0$, while for higher concentrations the absolute value of J has a particular evolution: it increases up to $x = 10$ mol% Cr_2O_3 and decreases thereafter. The decreasing of J value (Fig. 5) suggests more disordered local environments of Cr^{3+} ions for $x > 10$ mol% Cr_2O_3 , that determines the decrease of the exchange coupling intensity.

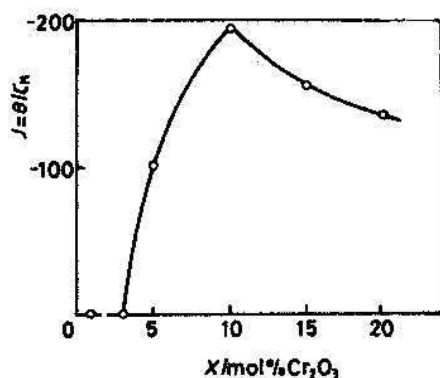


Fig. 5. Composition dependence of the molecular field constant, J .

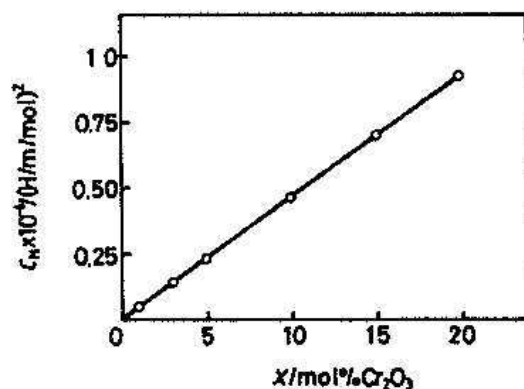


Fig. 6. Composition dependence of the molar Curie constant, C_M .

Table 1. Magnetic moment for system (1) glasses.

x [mol% Cr_2O_3]	μ_{eff} [μ_B]
1	3,87
3	3,87
5	3,87
10	3,86
15	3,89
20	3,85

The composition dependence of the molar Curie constant C_M is presented in Fig. 6. The values of the Curie constant, which are proportional to the ions concentration, linearly vary with the Cr_2O_3 content. According to Table 1, the experimental values of the effective magnetic moment $\mu_{\text{eff}} = (3.87 \pm 0.02)\mu_B$ are very close to the magnetic moment of Cr^{3+} ions in the free ion state, $\mu_{\text{Cr}^{3+}} = 3.87\mu_B$, in agreement with the values usually obtained in paramagnetic salts containing Cr ions [18].

3.2. EPR and magnetic susceptibility studies of glasses from system (2)

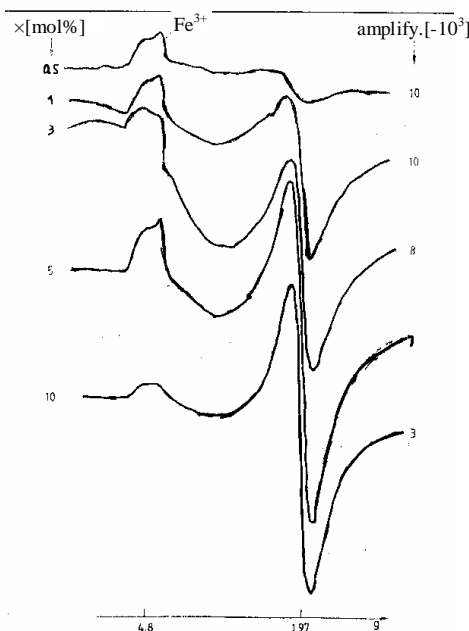


Fig. 7. EPR absorption spectra of Cr³⁺ ions in system (2).

All the investigated samples for this system show EPR absorption spectra due to the Cr³⁺ ions paramagnetic ions, presented in Fig. 7. The absorption line consists of two signals centered at $g \approx 4.8$, arising from isolated Cr³⁺ ions subjected to a strong orthorhombic crystalline field in a distorted octahedral environment, and another one at $g \approx 1.97$. The high-field absorption shows the superposition of signals at $g \approx 2.0$ and $g \approx 1.97$ (Fig. 7). As the Cr³⁺ ions concentration increases, the isolated ion vicinity is progressively altered and loses its well defined symmetry, the structural units involving Cr³⁺ ions in sites of strong crystalline field become less represented. The main feature of the spectrum for samples with $x \geq 1$ mol % Cr₂O₃ is the high field resonance line at $g \approx 1.97$. Its evolution was followed in the concentration dependence of the EPR parameters, line-width, ΔB , and the intensity was approximated by $J = I(\Delta B)^2$, where I denotes the line amplitude (height). These dependencies are presented in Figs. 8 and 9.

In contrast with low-field signal, the intensity of the $g \approx 1.97$ one gradually increases with the Cr₂O₃ content (Fig. 8).

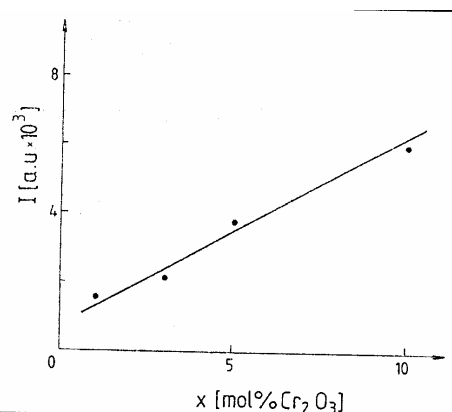


Fig. 8. Concentration dependence of the $g \approx 1.97$ line-intensity for system (2).

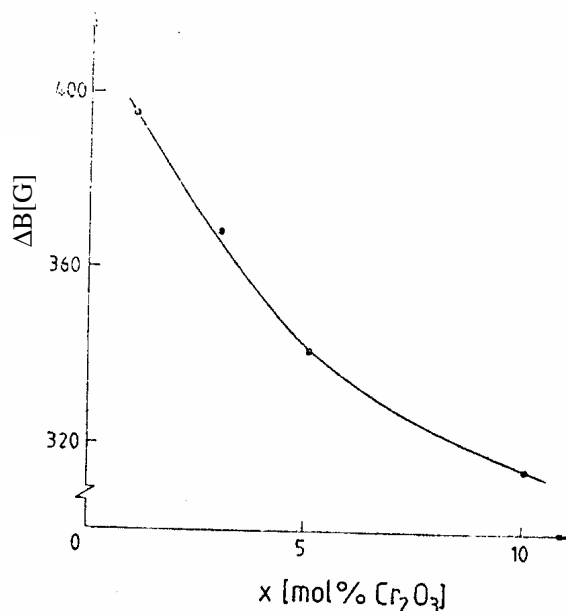


Fig. 9. Concentration dependence of the $g \approx 1.97$ line-width for system (2).

The temperature dependence of reciprocal magnetic susceptibility for system (2) obeys a Curie law, for $x \leq 1$ mol% Cr_2O_3 and a Curie-Weiss law for $x > 1$ mol% Cr_2O_3 . The values of the Curie temperature, θ_p , suggest an antiferromagnetic coupling of ions. The specific structure of the vitreous oxide solids imposes the short-range character of magnetic interactions and enhances the structural image of ionic clusters. The result agrees with the EPR data, explaining the $g \approx 1.97$ line narrowing as the result of super exchange interactions between ions involved in cluster structure [19].

Table 2. Molar constant and magnetic effective moment values for glasses of the system (2).

x [mol% Cr_2O_3]	C_M [emu/mol]	μ_{eff} [μ_B]
1	0.037228	3.86
3	0.111900	3.86
5	0.186676	3.87
10	0.377340	3.86

The experimental values estimated for the effective magnetic moment, μ_{eff} , are very close to the magnetic moment of Cr^{3+} in the free ion state: $\mu_{\text{Cr}^{3+}} = 3.87 \mu_B$ attesting the preponderance of this valence state of chromium ions in the studied glass.

3.3. EPR and magnetic susceptibility studies of glasses from system (3)

The absorption line for system (3), Fig. 10, consists of two signals centered at $g \approx 4.8$ and $g \approx 1.97$. The low field resonances, at $g \approx 4.8$ were attributed to isolated ions subjected to a strong orthorhombic crystalline field arising from a distorted octahedral environment. There is another one, centered at $g \approx 4.3$ due to a broad absorption attributed to Cr^{3+} ions in sites with a predominantly axial character [19]. For small concentrations, the high-field absorption shows the superposition of

signals at $g \approx 2.0$ and $g \approx 1.97$. The main feature of the spectrum for samples with $x \geq 1$ mol % Cr₂O₃ is the high field resonance line at $g \approx 1.97$. In contrast to the previously discussed signal, the intensity of the $g \approx 1.97$ increases as the Cr₂O₃ content of the sample rises to 20 mol%.

The concentration dependences of the EPR parameters, line-width and the intensity, show exchange interaction narrowing, very pronounced within $1 < x \leq 10$ mol % Cr₂O₃. For $x > 10$ mol % Cr₂O₃, the narrowing is stopped by the broadening effects of the increased disorder in the matrix due to large doping levels. The evolution of the EPR parameters suggests the cluster association of Cr³⁺ ions.

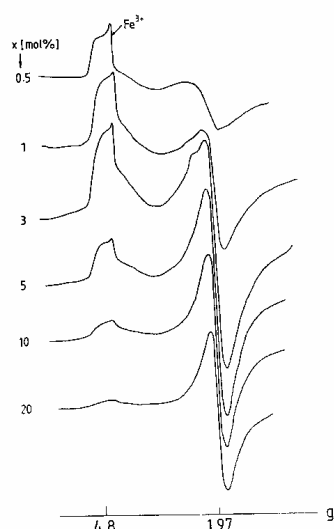


Fig. 10. EPR absorption spectra in system (3).

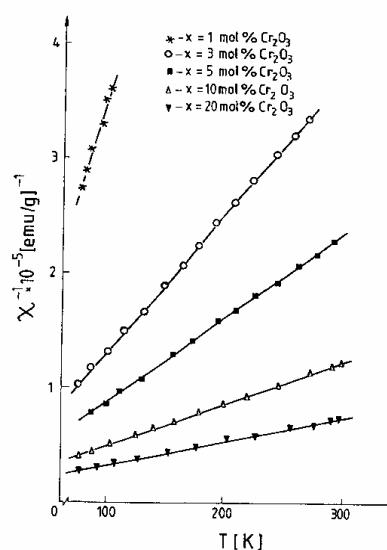


Fig. 11. Temperature dependence of the reciprocal magnetic susceptibility for system (3).

For $x > 1$ mol% Cr₂O₃, the reciprocal magnetic susceptibility obeys a Curie-Weiss law with negative paramagnetic Curie temperature, θ_p , characteristic to antiferromagnetic coupling of magnetic ions. The absolute value of θ_p increases for $x > 1$ mol% with the magnetic content of the sample, in agreement with theoretical data 19. The values of the molar Curie constant, C_M (Table 3), are proportional to the Cr³⁺ ion concentration.

Table 3. Magnetic moment, paramagnetic Curie temperature and molar Curie constant for glasses of the system (3).

x [mol% Cr ₂ O ₃]	μ_{eff} [μ_B]	θ_p [K]	C_M [emu/mol]
1	3.85	0	0.03704
3	3.86	-6	0.11139
5	3.85	-15	0.18662
10	3.85	-27	0.37043
20	3.85	-38	0.74181

The experimental values estimated for the effective magnetic moment, μ_{eff} are very close to the magnetic moment of Cr³⁺ in the free ion state: $\mu_{\text{Cr}^{3+}} = 3.87 \mu_B$ attesting the preponderance of this valence state of chromium ions in the studied glass.

4. Conclusions

The EPR spectra due to the Cr^{3+} ions in vitreous matrix revealed the structural details of the diamagnetic host, the coordination and the distribution of these ions, the EPR parameters being sensitive to the local symmetry, the character of the chemical bonds as well as of the structural factors.

EPR and magnetic susceptibility data have shown that the Cr^{3+} ions are present in the studied glasses as isolated species, coupled by dipol-dipol and/or negative superexchange interactions. The strength of these interactions was determined in function of x and different modifiers of vitreous matrix.

The line-width reaches smaller values for system (2) than those corresponding to system (3) prepared in similar conditions. This suggests more intense interactions between Cr^{3+} ions for glasses containing oxygen ligand ions than those corresponding to matrices where oxygen was partially replaced by fluorine.

The absolute values of θ_p for system (2) are larger than those corresponding to system (3), result which supports the EPR line-width data, comparatively shown for these two vitreous systems.

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