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An electron-spin resonance investigation of vitreous and crystalline modifications of germanium dioxide

A. A. MARGARYAN
218 E Chevy Chase Drive, Suite 8, Glendale, CA 91205, USA

Glass matrices on basic GeO_2 are of interest in connection with the increasing interest in glass as the new materials for optics and fibre optics [1]. Glass former–activator and crystal–activator compositions are of considerable interest for elucidating the structure and bonding in vitreous (isotropic) and crystalline (anisotropic) systems. Information about the behaviour of the activator in these matrices can be obtained from electron-spin resonance (ESR) signals.

We used divalent manganese as the activator; Mn^{2+} is a sensitive indicator of structural changes owing to its unshielded d^5 orbitals. The paramagnetic spectra observed from Mn^{2+} usually correspond to electron-spin transitions of the type $-1/2 \leftrightarrow +1/2$ and to band values of $g = 4.27$ and $g = 2.00$ [2, 3]. Previously, we used ESR to investigate the SiO_2–Mn^{2+} system [4, 5]. We established that the short-range symmetry elements around the Mn^{2+} are the same in the vitreous and crystalline states of SiO_2 and that their ESR spectra are described by the same parameters.

The vitreous and crystalline (hexagonal) forms of GeO_2 activated by Mn^{2+} were prepared by the method described in [5]. The ESR spectra were operating at a frequency of 9370 MHz at 295 K. The manganese was introduced into the matrix in the form of MnO_2 in amounts of 0.05–2 or of 0.03–1.2 wt % Mn^{2+} (with respect to the GeO_2).

The ESR signal from Mn^{2+} in vitreous and crystalline GeO_2 are shown in Fig. 1.

To judge from existing work [6–11] devoted to investigating vitreous and crystalline GeO_2, GeO_2 has been studied very little on the level of chemical-bond and ligand-field theory.

At present there are two contradictory hypotheses [6, 12] to explain the structure of germanate glasses. This means that serious difficulties are involved in interpreting the results of physical and physicochemical measurements for glasses based on GeO_2.

The important thing is to find out the degree of covalent bonding between the maganese and ligand in GeO_2, the strength of the ligand field, the co-ordinative position of the Mn^{2+} and the degree of order in the structure of the GeO_2 in its vitreous and crystalline states [13–15]. The ESR results (Fig. 1) show that at low concentrations the d-orbitals of the central ion (Mn^{2+}) interact differently with the co-ordinatable ligands in vitreous and crystalline GeO_2 (curves 1, 2, 6 and 7).

Thus, we are dealing with local environments

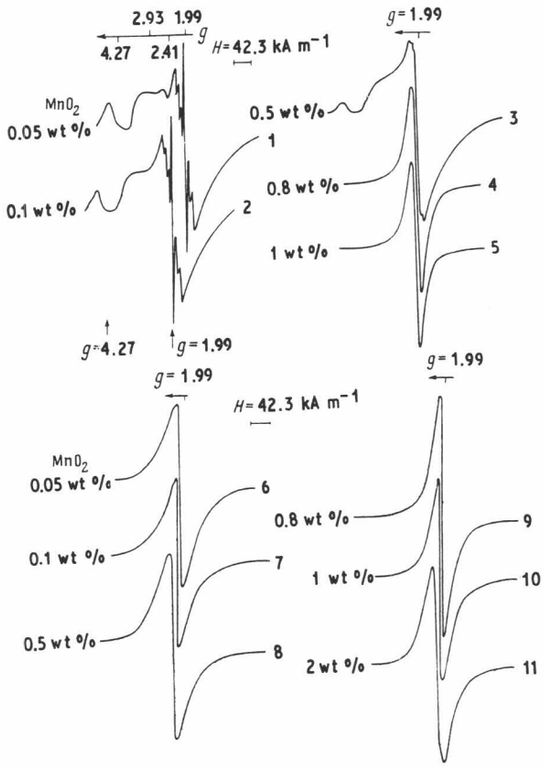

Figure 1 ESR spectra of Mn^{2+} in vitreous (curves 1–5) and crystalline (hexagonal forms) (curves 6–11) GeO_2.

around Mn^{2+} consisting of GeO_2 in different structural compositions. Any change in the solvate cloud will lead to some difference in the ESR spectra of the Mn^{2+} (curves 1, 2, 3 and 4).

We determined the hyperfine splitting (A) for Mn^{2+} (concentration 0.03 wt %) in vitreous GeO_2 to be 7.60 kA m^{-1}. When the concentration of Mn^{2+} is increased (curves 1, 2 and 3), the width of the six lines increases and they coalesce into one broad line (curves 4 and 5, with $g = 1.99$). As the measurements show, the hyperfine splitting decreases at high manganese concentrations due to exchange between the electron spins of adjacent manganese ions. As a rule, exchange decreases hyperfine splitting. The latter depends to a great extent on the type of matrix in which the manganese ions are diluted or contained [16–18].

An important role here is played by the proportion of one or other type of bonding existing between the ligand and glass-former ions and the ligand and activator ions in the structure [1].

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In [19, 20] the dependence between the melting point of several oxides and the strength of their field is reported. This dependence passes through a region in which the oxides have high melting points (having ionic bonding), then falls into the region of glass-forming oxides and ends up in a region where the oxides have very low melting points. The latter have a covalent structure, and the glass-formers have both types of bond. However, GeO_2 is closer to the covalent region (the melting point of GeO_2 is 1116 °C) than SiO_2 (melting point 1700 °C), so the proportion of covalency in the Ge–O bond is greater than in the Si–O bond.

Proceeding from the ESR data for Mn^{2+}, we can conclude that the degree of hyperfine splitting in a covalent ligand–activator interaction is lower than that in an ionic bond. The hyperfine splitting for Mn^{2+} is directly proportional to the degree of ionic bonding in the ligand–activator bond [21–23].

It has been found [24,25] that the ESR spectra of transition metals, particularly Mn^{2+}, in organic and inorganic solvents have a more resolved and split structure when the samples are in a vitreous state than when they are in a polycrystalline state (Figs 2 and 3).

In the vitreous form, the structural elements of a substance are preferentially involved in covalent interactions (owing to sp^n hybridization) compared with the crystalline form.

A comparison of the ESR spectra of Mn^{2+} in vitreous (curves 1 and 2) and crystalline (curves 6 and 7) germanium dioxide (Fig. 1) shows them to be identical to the data in [24, 25] (Figs 2 and 3). The bands in the spectra of vitreous GeO_2 (curves 1 and 2; Fig. 1) are of interest.

Together with the hyperfine splitting, new solvate structures are formed around the Mn^{2+} with tensor values of $g = 2.41$, 2.93 and 4.27. This confirms that there is fluctuation of the oxygen in the co-ordination sphere of the germanium in the vitreous form of GeO_2.

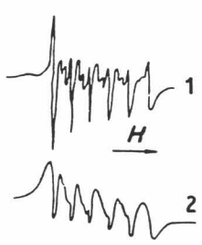

Figure 2 ESR spectra of Mn^{2+} in vitreous (curve 1) and polycrystalline (curve 2) methanol [24].

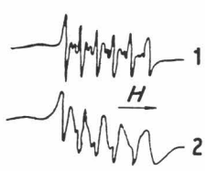

Figure 3 ESR spectra of Mn^{2+} in vitreous (curve 1) and polycrystalline (curve 2) 12 M HCl [24].

The presence of germanium–oxygen structures with equivalent compositions with respect to oxygen gives rise to new environments in the field of the paramagnetic centre.

At MnO_2 concentrations of 0.8 wt % or more the bands mentioned above disappear, leaving a single line with $g = 1.99$.

The oxygen introduced into the glass matrix the MnO_2 (R_xO_y) levels out the non-uniformity or heterogeneity of the oxygen distribution in the structure of the vitreous GeO_2. This levelling-out process is accompanied by a change in the co-ordination of the germanium (higher co-ordinations are converted into tetrahedra) and the density and free volume change simultaneously. This gives rise to the anomalous physical and physicochemical properties of germanate glasses.

In structural respects the vitreous form of GeO_2 (curves 1, 2 and 3) must be non-uniform in comparison with the matrices (curves 4 and 5; Fig. 1). This is confirmed by electron microscopic investigations of the samples (Fig. 4a to d corresponds to curves 1, 2, 3 and 5, respectively, in Fig. 1).

Heterogeneous-phase sections with pronounced non-uniformity can be clearly distinguished in Fig. 4a and b. At a MnO_2 concentration of 0.5 wt % (Fig. 4c) drops of the same type in a general phase separation can be observed. In the case of 1.0 wt % MnO_2 (Fig. 4d) there are agglomerates of the same size and of uniform structure.

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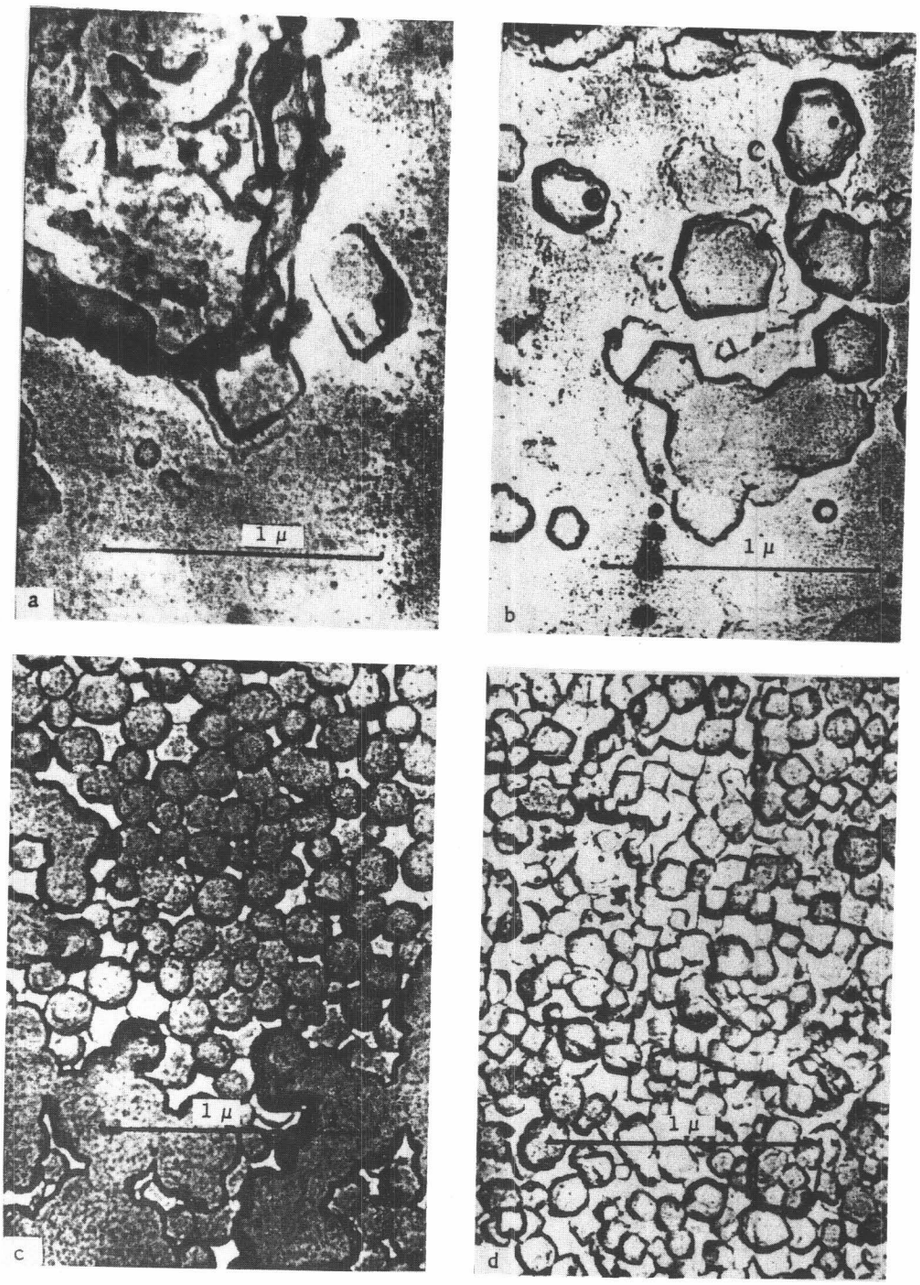

Figure 4 Electron micrographs of vitreous GeO_2: microstructure of glasses containing MnO_2 in amounts of (a) 0.05, (b) 0.1, (c) 0.5 and (d) 1.0 mol %. Magnification 40 000 ×.

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