EXAFS AND XANES STUDIES OF LOCAL ORDER IN OXIDE GLASSES: MANGANESE IMPURITY DEFECTS AND VANADIUM LOW-SYMMETRY COMPLEXES

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The local order in oxide glasses has been studied by means of the EXAFS and XANES techniques. It has been established that manganese impurity defects enter the germanium phosphate glasses in a two-valent state in the form of MnO_6 octahedra with a Mn–O distance of 2.05 Å. In the vanadium phosphate glasses low symmetry complexes of V atoms are present. In these complexes the shorter bond length corresponds well with the double V–O distance in V_2O_5, whereas the average distance of the four O atoms placed in a plane is 0.15 Å longer than the corresponding distance in the crystalline V_2O_5. Besides, VO_4 tetrahedra with a V–O distance of 1.75 Å are present.

1. Introduction

Extended X-ray absorption fine structure (EXAFS) is a modern structural technique for solid state studies [1]. In comparison with X-ray, electron and neutron scattering methods, EXAFS can be successfully applied both to crystalline and non-crystalline materials. In the last few years, EXAFS and absorption near edge structure (XANES) studies carried out with synchrotron radiation have began to add to our knowledge of the local order in glasses [1,2].

Models of local ordering in glasses are mainly based on scattering data of X-rays, electrons and neutrons and significant progress has been made in the understanding of the local environment of single component glasses [3]. However, these methods have a number of restrictions due to the fact that the radial distribution function (RDF) contains all the possible pair distances among the atoms, i.e. $F(R) = \Sigma_i F_i(R)$, where $F_i(R)$ is the partial RDF of the ith type atom. It is hardly possible to undo such a RDF in multi-component glasses [3]. The EXAFS method, selectively exciting the ith type atom, allows one to obtain its partial RDF. Thus the investigation of sodium and calcium silicate glasses made it possible to conclude about the non-adequacy of the Zachariasen model for ion modifiers [2]. It is now clear that ion modifiers have highly-ordered near-neighbour surroundings with weak scattering from

metal–oxygen bonds and that they form an intrinsic disordered net.

The high resolving power of EXAFS allows to study more precisely the distribution of distances in the first coordination sphere, i.e. to determine the different types of bond lengths in low-symmetry complexes and their static and dynamic distribution. However, the EXAFS method is less sensitive to the farther coordination spheres [1,2]. Special interest in turned to study the local structure of impurity defects in glasses [4]. The knowledge of the near-neighbour bond lengths is important to select the correct model for the impurity centers and to calculate the properties of the glassy material. The sensitivity of the fluorescent method reaches $10^{-4}\%$, which is enough to investigate impurity defects in glasses and crystals at concentrations of defects lower than $10^{19}\,cm^{-3}$ [5]. Therefore we have investigated Mn impurity defects (at a concentration $10^{19}\,cm^{-3}$) in germanium–phosphate glasses with the fluorescence EXAFS technique. The low-symmetry centres of vanadium complexes have also been investigated in these glasses. Complementary information needed for the analysis of the EXAFS spectra – number and type of centres, symmetry of centres, etc. – has been obtained from EPR measurements made on the same materials [6].

2. Experiment and data processing

The experiments have been performed at the X-ray beam line of the Frascati, Italy, synchrotron radiation facility PULS. The storage ring ADONE was operated at an energy of 1.5 GeV and the typical electron current was 50 mA. The radiation was monochromatized by a channel-cut Si (220) or Si (111) crystal with an energy resolution of about 0.2 and 0.5 eV respectively. The measured glass samples were powdered to dimensions of a few μm and mixed with a small amount the HBO_3. The measurements were performed at room temperature. The vanadium spectra were measured in transmission, whereas the manganese spectra were measured in the fluorescent mode [7].

The analysis of the EXAFS data is done as follows. After a Victoreen fit to substract the absorption background, a polynomial fit is used to extract the oscillating part of the atomic absorption coefficient, i.e. the EXAFS $\chi(k)$ function. In order to get the best subtraction of the low-frequency oscillations, we multiply the $\chi(k)$ function by a given power n of the k wave vector, and then we perform a further polynomial (3rd degree) fit which is then subtracted to give the final $\chi(k) \cdot k$ function. The spectra are then Fourier-transformed by using a Hanning window function to give the radial distribution function $F(r)$ around the excited atom.

In the single scattering approximation for the K-shell excitation, the $\chi(k) \cdot k$ has the following well-known expression:

$$\chi(k)k = \sum_j \frac{N_j}{kR_j} f_j(k) \sin\left(2kR_j + 2\phi_j(k)\right) \exp\left(-2\sigma_j^2 k^2\right) \exp\left(-R_j/\lambda\right),$$

$$(1)$$

where N_j is the number of neighbours of type j at neighbour distance R_j, σ_j is the Debye–Waller factor, $f_j(k)$ is the amplitude of the backscattered wave, and λ_j is the mean free path of the photoelectron. The threshold energy E_0 was taken at the first inflection point of the absorption edge from Mn and at the peak of the white line for V, respectively. The calculated values of Teo and Lee [8] for the scattering amplitudes $f_j(k)$ and the phase shifts $\phi_j(k)$ were employed to fit the experimental spectra. For comparison the phase shift extracted from a model crystal was also used. The EPR spectra were taken at room temperature with an X-band spectrometer.

3. Results and discussion

3.1. Impurity defects of manganese

EXAFS and XANES spectra were collected above the Mn–K edge in two different glasses $95GeO_2 \cdot 5P_2O_5$ and $75GeO_2 \cdot 25P_2O_5$ containing 0.1 mol% of MnO_2. The XANES spectra of the two samples practically do not differ and are presented in fig. 1. The spectral shape is typical of Mn^{2+} ions in disordered oxygen compounds [9], and the position of the A, B, C and D peaks and shoulders coincides well with the position of the corresponding peaks in MnO, where Mn^{2+} is in octahedral coordination. It is known [9] that the amplitude of the peak A, corresponding to the dipole-forbidden $1s \rightarrow 3d$ transition, should be observable if Mn^{2+} occupies a non-centrosymmetric position. It can be concluded, on the basis of XANES data, that Mn ions are in a divalent state close to the centrosymmetric position in the oxygen octahedral surroundings.

A typical partial RDF of the Mn^{2+} ions obtained from the Fourier transformation of $\chi(k)$ in the 2–10 Å^{-1} interval is shown in fig. 2. The first

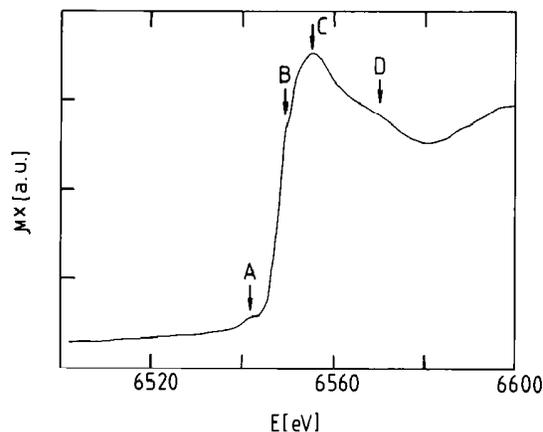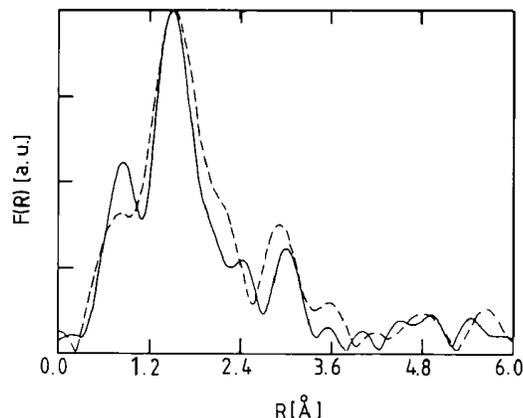Fig. 1. Near-edge K spectrum of Mn in $95GeO_2 \cdot 5P_2O_5$.

Fig. 2. Fourier transform of $\chi(k)$ above the Mn K edge in doped Ge phosphate glasses (0.1% MnO_2). Dotted line: 5% P_2O_5; full line: 25% P_2O_5.

peak at ≈ 1.5 Å, corresponding to the shortest Mn–O distance, is clearly seen. The fitting of the $\chi(k)$ function using the Teo and Lee values [8] gives a distance of 2.03 ± 0.03 Å. In crystalline Mn–O we obtain 2.05 ± 0.03 Å. This distance is 0.15–0.17 Å shorter than the typical distances of octahedral complexes of manganese in crystalline compounds.

In EPR spectra [6] we observed a typical spectrum of Mn^{2+} ions with a broad line in the $g = 2.0$ region, a shoulder in the $g = 3$ region and a weakly resolved hyperfine structure at $g = 2.0$ and $g = 4.3$. Undoubtedly, the main part of the manganese ions gives rise to the $g \approx 2$ line. Consequently, the broad EPR line corresponds to the Mn^{2+} ions situated in the centrosymmetric octahedral position, as found above. The other types of manganese ions centres, which give narrow lines at $g = 2.0$ and $g = 4.3$ and which are interpreted as rhombic centres with a weak and strong crystalline field, respectively, constitute an insignificant part of the total number of manganese ions. It will be therefore of interest to apply EXAFS and XANES techniques to glasses in which rhombic centres with $g = 2$ and $g = 4.3$ prevail over other centres. Our data on the near-neighbour environment of defect Mn impurities compare well with those of manganese ions in oxide glasses at high concentrations of Mn [10]. In both cases there is a characteristic tendency towards a shortening of the Mn–O bond in oxide glasses in comparison with crystals. In the EPR spectra of manganese the hyperfine-structure constant decreases with decreasing the Mn–O bond length [11]. On the basis of the EXAFS data we conclude that the previously observed [6] decrease of the hyperfine constant at the crystal–glass transition can be related to the decrease of the Mn–O distance. EXAFS data allow us to draw a series of additional conclusions about the inclusion of MnO_6 octahedra into the glass network. The presence of a peak at about 3.0 Å in the RDF (fig. 2) points to definite distances in the second coordination sphere of manganese. In multicomponent germanium
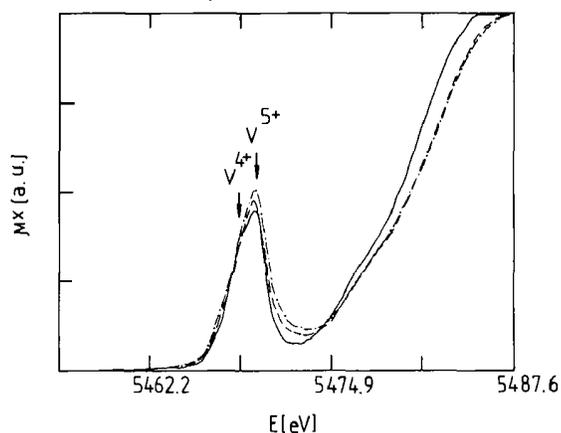
Fig. 3. Near-edge K spectrum of V in vanadium phosphate glasses (————0.1, - - - - - -0.5, ·—·—·0.7).

glasses [12] the peaks corresponding to the Ge–P and Ge–Ge distances are not observed, i.e. the second-neighbour peak smears completely because of the compositional disorder. On the other hand, the wide line observed in the EPR spectrum points to the clustering of manganese ions. Therefore we suggest that the peak at 3.0 Å is due to the Mn–Mn backscattering. The best agreement in the modelling of the EXAFS spectrum is achieved for $N = 2$ and $\sigma = 0.05$ Å.

3.2. Vanadium phosphate glasses

We have measured the V–K edge in the following glasses $10V_2O_5 \cdot 20GeO_2 \cdot 70P_2O_5$, $20V_2O_5 \cdot 20GeO_2 \cdot 60P_2O_5$, $30V_2O_5 \cdot 20GeO_2 \cdot 50P_2O_5$, $40V_2O_5 \cdot 20GeO_2 \cdot 40P_2O_5$, $50V_2O_5 \cdot 20GeO_2 \cdot 30P_2O_5$, $60V_2O_5 \cdot 20GeO_2 \cdot 20P_2O_5$, $70V_2O_5 \cdot 20GeO_2 \cdot 10P_2O_5$. For comparison we have used crystalline V_2O_5 data [13]. The peak below the K edge onset (fig. 3) is due to the absorption of vanadium atoms located in a noncentrosymmetric site symmetry [13,14]; namely, the presence of vanadium oxocomplexes with a short double bond V=O leads to the appearance of this peak. Besides, its shape is described by the superposition of two peaks corresponding to two valent states V^{4+} and V^{5+}. Thus, it can be concluded that in glasses the vanadium ions are situated in noncentrosymmetric position with one or two shortened V=O bonds. The partial RDFs obtained from Fourier transforming $\chi(k) \cdot k^2$ in the 2–11 Å^{-1} range are presented in fig. 4. In the range of distances corresponding to the first coordination sphere, three well-pronounced peaks are observed. The $\chi(k) \cdot k^2$ spectra obtained by the reverse Fourier transformation in the 0.3–2.1 Å range (characterizing the first coordination sphere of vanadium ions) are shown in fig. 5. Detailed results can be obtained by modelling the shapes of the $\chi(k) \cdot k^2$ spectra and the RDF. The best agreement is achieved for three different V–O distances: 1.35 ± 0.05 Å (up to $N = 0.3$ O atoms), 1.55 ± 0.05 Å

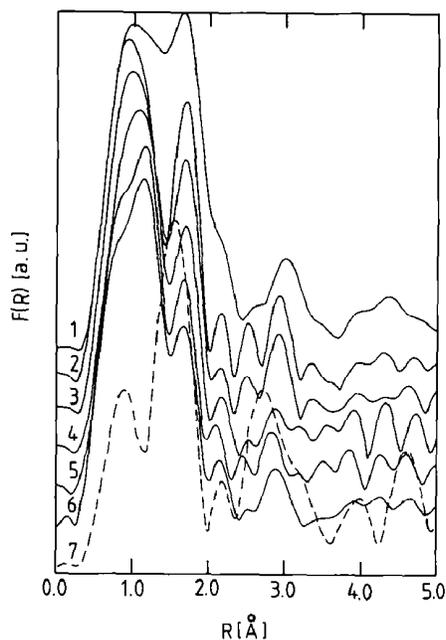Fig. 4. Fourier Transform of the EXAFS $\chi(k)k^2$ function in the $2-11$ Å^{-1} interval around the V K-edge for $(x)V_2O_5 \cdot 20GeO_2 \cdot (80-x)P_2O_5$. $x = 20$ (1), $x = 30$ (2), $x = 40$ (3), $x = 50$ (4), $x = 60$ (5), $x = 70$ (6), V_2O_5 crystal (7).
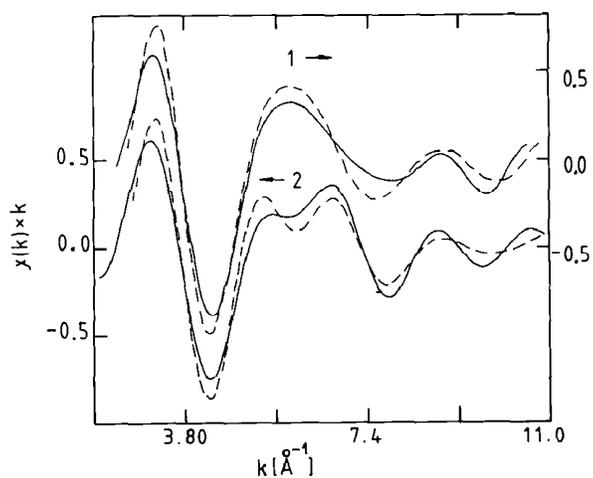

Fig. 5. Backfourier transform of vanadium phosphate glasses between $R = 0.3$ and 2.1 Å (solid curves) and the corresponding simulations using Teo and Lee phases (dashed curves). (1) 70% V_2O_5; (2) 30% V_2O_5.

(up to $N = 0.7$ O atoms) and 2.25 ± 0.05 Å (up to $N = 4$ O atoms). Accordingly, the Debye–Waller factor is 0.08 Å for the first two distances and changes from 0.15 to 0.2 Å for the third distance in a series of glasses at increasing V_2O_5 content. For crystalline V_2O_5 we have established that the best agreement with the experiment is achieved for two V–O distances, 1.35 ± 0.05 Å ($N = 1$) and 2.1 ± 0.05 Å ($N = 4$). It is also possible that one more oxygen, situated at a distance 2.6 ± 0.1 Å contributes to the spectrum. It is natural to assign the distance 1.35 Å to the shortest bondlength of V_2O_5, which is 1.58 Å. The difference in the distances can be explained by the uncertainty in the phase shifts $\phi_i(k)$ for the V=O bond [8]. Actually, for this bond the electron charge is concentrated between the atoms and thus the assumed spherical distribution for the electron density (when calculating phase shifts) might give rise to a shorter bond length. In this case, we should consider different phase shifts, backscattering amplitudes and threshold energies for the different subshells. The other V–O distance must correspond to the remaining four distances 1.77, 1.88, 1.88 and 2.02 Å (the distance 2.7 Å corresponds to the oxygen atoms in the neighbouring layer which is rather weakly felt in the experiment). Thus our interpretation of the results for the vanadium phosphate glasses is the following. The 1.35 Å bond length is determined by the double V–O bond which is identical to that in crystalline V_2O_5 ($R = 1.58$ Å). Such bond lengths are most clearly seen at high concentrations (60–70%) of V_2O_5 in the glasses. The other vanadium–oxygen bond at 1.55 Å may correspond to the V–O distance $R = 1.75 \pm 0.05$ Å. Perhaps these are the tetrahedral oxygen complexes of vanadium. The 2.25 Å distance may correspond to distances up to four oxygen atoms situated in a plane. It is interesting to note that the dispersion of the distance ($\sigma = 0.08$ Å) for the shortest and strongest V–O bond is much less than that of the basal V–O bonds ($\sigma = 0.15$–0.2 Å). The latter values are comparable with the different V–O distances in V_2O_5.

To solve the question of the building-in of vanadium oxygen complexes into the glass network it is necessary to discuss the peaks in the 3–4 Å region of the RDF. The modelling of the $\chi(k)k^2$ and of the RDF functions in crystalline V_2O_5 shows that the peak in this region may correspond to the V–V distances. Accordingly, the 3.15 ± 0.05 Å and 3.4 ± 0.05 Å distances approximate roughly the distance 3.25 ± 0.05 Å to four vanadium atoms. In the glassy state this peak is considerably weaker than in the crystal. This may depend either on the compositional disorder of the structure, in which, a random net of vanadium, phosphor and germanium polyhedra is formed or to a broader distribution of V–V bondlengths in glasses than in crystals. Undoubtedly, the contribution of the vanadium polyhedra connected through the edges is prevailing. There is an evidence of a shortening (≈ 0.15 Å) of the V–V distance in glasses by increasing the V_2O_5 content.

In the EPR spectra of vanadium glasses we have observed an intense signal from the V^{4+} ions in the $g = 2$ region of the Lorentz shape with $dH = 250$ G. Such a signal can be associated to the exchange coupling of the paramagnetic

vanadium ions. This is corroborated by the existence of well-defined V–V bond lengths in the glasses. At low V_2O_5 concentration, beside the broad structure at $g = 2$, sharp lines are observed in the EPR spectra which are usually ascribed to isolated V^{4+} ions in the axial surrounding. However, due to their relatively small number, these centers are not seen in EXAFS and XANES spectra.

4. Conclusion

The application of the EXAFS and XANES methods allows us to obtain detailed information on the local surroundings of impurity defects in glasses and their distribution in the glass network. It is established that manganese impurity defects enter the germanium phosphate glasses in a two-valent state in the form of oxygen octahedra with a Mn–O distance of 2.05 Å – essentially smaller than the Mn–O octahedral distance in crystals – and occupy the centrosymmetric position. In the case of vanadium phosphate glasses we have found that the VO_6 octahedral complexes of vanadium oxide are present in the glasses which are equivalent to the vanadium complexes in crystalline V_2O_5 with one short double bond at 1.6 Å. The average V–O distance to the four atoms placed in the plane is 0.15 Å longer than the corresponding average distance in crystalline V_2O_5. Besides, tetrahedral VO_4 complexes of vanadium oxide with a V–O distance of 1.75 Å are present. Moreover, polyhedra of vanadium oxide with a mean V–V distance of 3.2 Å are connected through their edges.

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