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EXAFS/XANES studies of the local structure of amorphous ionic and electronic-ionic conductors

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X-ray absorption spectroscopy methods such as EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near Edge Structure) are sophisticated and effective tools for studying the local structure of many solids and liquids. Their use is particularly valuable in the case of amorphous systems, in which due to the absence of long-range order the possibilities of structure determination by diffraction methods are limited. EXAFS and XANES have been extensively used to study the local structure of many electrically conducting (via ions, electrons, or both electrons and ions) solids. The special merit of the latter studies is that their results reveal the short-range structure of these conductors, which is an important factor determining their transport properties. The paper reports recent results of EXAFS/XANES studies on the local structure of selected electrically conducting glasses of the Li_2O $–V_2O_5–P_2O_5$ system and their silver analogues. All spectra were acquired at the K-edge of vanadium.

Key words: *EXAFS; XANES; amorphous ionic conductor; local structure; vanadate glass*

1. Introduction

During over thirty years of progress in the field of solid-state ionics it has been established that the transport of ions and electrons in electrically conducting solids is strongly dependent on the structure of the conducting materials (cf. recent review by Hull [1]). Structural studies are relatively straightforward in the case of crystalline materials, where one can apply the powerful method of X-ray diffractometry (XRD). The structure determination of amorphous solids is more difficult due to absence of long-range order in these materials, which makes XRD much less efficient. There are, however, several spectroscopic methods, such as Raman scattering, infrared absorption (IR), and electron paramagnetic resonance (EPR), which can provide information on the local structure of these solids.

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An important group of such methods is X-ray absorption spectroscopy (XAS). The most widely applied of them are EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure), sometimes jointly called XAFS (X-ray absorption fine structure).

Throughout the years XAFS methods have been used to study a large number of systems: solid, liquid, and gaseous. The main advantages of the methods compared to other spectroscopies are: their selectivity (they probe the vicinity of a given central atom that absorbs X-rays up to a few Å), insensitivity to long-range order, the possibility of determining the basic parameters of several of the closest coordination shells (the number of atoms in each shell, distances, multiple scattering paths, etc.) [2]. Additionally, XANES spectra in the immediate proximity of the absorption edge are sensitive to the formal state of oxidation of transition metal atoms, to the symmetry of the cage formed around the central absorbing atom by its nearest neighbours, to details on atomic or molecular orbitals, to allowed and forbidden transitions of the central atom, etc. Among the systems investigated by XAFS methods, there have been also ionic and mixed electronic-ionic solid conductors, such as e.g., α- and β-AgI and silver borate glasses [3, 4], bismuth oxides, and BIMEVOX-es [5, 6] or V_2O_5, and vanadate glasses or gels [7, 8].

In this paper, we present the results of our XANES studies on lithium vanadate -phosphate glasses, which are known to be mixed electronic-ionic conductors (cf. e.g. Ref. [10]), and on their analogues with lithium replaced by silver.

2. Experimental

Lithium and silver vanadate and vanadate-phosphate glasses were prepared by a standard press-quenching technique [10] from dried reagent-grade chemicals: $AgNO_3$ (POCh), $LiNO_3$ (Aldrich), V_2O_5 (ABCR), $NH_4H_2PO_4$ (POCh). The compositions of the series of lithium-containing glasses may be described by the general formula $x Li_2O \cdot (100 - 2x) V_2O_5 \cdot x P_2O_5$, where x = 15, 35, and 45. Silver glasses had the composition described by an analogous formula, namely $x Ag_2O \cdot (100 - 2x) V_2O_5 \cdot x P_2O_5$, where x = 15 and 35. Additionally, we carried out XAFS studies on a reference material – commercial crystalline V_2O_5 powder (ABCR, reagent grade).

As-received glasses, prior to XAFS measurements, were routinely characterized by X-ray diffractometry (XRD), which confirmed the absence of crystalline phases.

Before XAFS measurements, samples were ground in an agate mortar to a uniform powder. The powder was evenly distributed on a Scotch adhesive tape and covered with another piece of adhesive tape. The resulting “sandwiches” were mounted on a sample holder. All measurements were done at room temperature.

XAFS experiments were carried out on a A1 station at the Hasylab synchrotron facility in Hamburg. The X-ray energy range near the K-edge of vanadium (5465 eV) was used. The radiation was monochromatized by a Si (111) monochromator set

either in a standard 2-crystal mode or a in a special 4-crystal mode (for some runs of XANES). The latter mode was used to improve the energy resolution of the incident beam (below 0.5 eV). The studies were done in transmission mode using ionisation chambers as detectors of incident and transmitted radiation.

3. Results

Lithium vanadate-phosphate glasses. The XAFS spectra of glasses with a composition of $x\mathrm{Li_2O}\cdot(100 - 2x)\mathrm{V_2O_5}\cdot x\mathrm{P_2O_5}$ contain several characteristic features: a strong pre-peak, an absorption edge and an oscillatory part above the edge. The absorbance modulations are stronger close to the edge and are damped at higher energies. The fast decay of the oscillations in the EXAFS signals observed for most of the studied glasses led to difficulties in obtaining reliable values for interatomic distances of the secondary and further coordination shells as well as other parameters characterizing local structure. An overview of the EXAFS studies of these glasses will be presented in a separate paper. Herein, we focus on presenting the results of the absorption spectra in the XANES region, i.e. approximately in the 5460–5540 eV range.

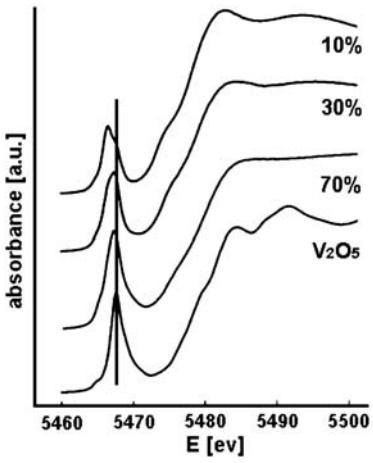

Fig. 1. XANES spectra of glasses with the composition of $x\mathrm{Li_2O}\cdot(100 - 2x)\mathrm{V_2O_5}\cdot x\mathrm{P_2O_5}$, where x = 15, 35, 45, taken at the K-edge of vanadium. The numbers next to the curves denote the molar fraction of $\mathrm{V_2O_5}$. The vertical line at the pre-edge peak serves to emphasize the position shift

Figure 1 shows the XANES region of the spectra for the studied lithium vanadate -phosphate glasses. As the amount of $\mathrm{V_2O_5}$ increases, several changes are observed: i) the pre-peak systematically shifts towards higher energies and visibly changes its shape, ii) there is some shift of the position of the absorption edge, iii) modulations above the edge, which are well discernible for crystalline $\mathrm{V_2O_5}$, are absent in the case of the investigated glasses.

Lithium vs. silver vanadate-phosphate glasses. In Figure 2, the XANES spectrum for the glass $15\mathrm{Li_2O}\cdot70\mathrm{V_2O_5}\cdot15\mathrm{P_2O_5}$ is presented, along with its silver analogue $15\mathrm{Ag_2O}\cdot70\mathrm{V_2O_5}\cdot15\mathrm{P_2O_5}$ and a reference sample – crystalline $\mathrm{V_2O_5}$. The spectra of

both glasses are identical. In both cases, the pre-peak has the same position, height, and shape. Also, above the absorption edge the spectra are similarly flat, without any discernible modulation, in opposition to the spectrum of crystalline V_2O_5, in which oscillations are well visible in this range.

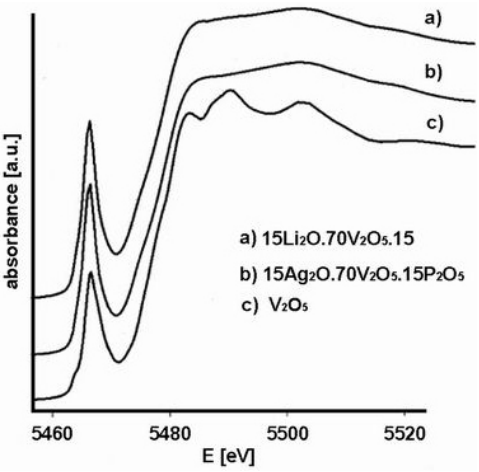

Fig. 2. XANES spectra of glasses with compositions of $15Li_2O{\cdot}70V_2O_5{\cdot}15P_2O_5$ and $15Ag_2O{\cdot}70V_2O_5{\cdot}15P_2O_5$, and of crystalline V_2O_5

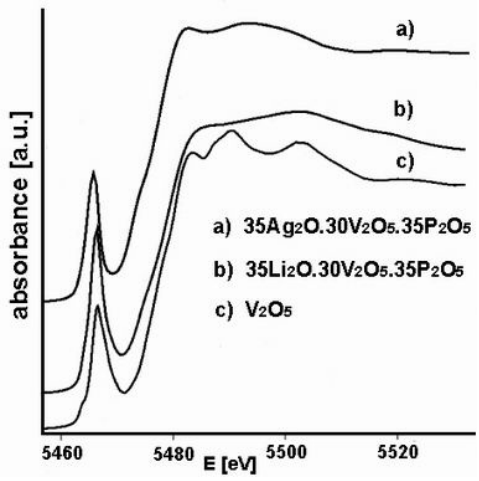

Fig. 3. XANES spectra of glasses with compositions of $35Li_2O{\cdot}30V_2O_5{\cdot}35P_2O_5$ and $35Ag_2O{\cdot}30V_2O_5{\cdot}35P_2O_5$, and of crystalline V_2O_5

The differences between the spectra obtained for lithium- and silver glasses appear when the amount of the modifier is higher (35 mol %) (Fig. 3). The position of the pre-edge peak for the $35Ag_2O{\cdot}30V_2O_5{\cdot}35P_2O_5$ glass is shifted towards lower energies compared to its lithium analogue. Additionally, there are weak, but discernible oscillations above the absorption edge for the silver glass, while a plateau is observed for the lithium glass.

4. Discussion

A strong pre-edge peak visible in all the spectra in Figure 1 is due to a 1s–3d electronic transition in the vanadium atom [7]. This transition is forbidden for the vanadium atom in an octahedral environment, but becomes allowed if the symmetry is lowered. In crystalline V_2O_5, the oxygen atoms around vanadium V^{5+} form a distorted pyramid with a square base [8]. The distances between the central vanadium atom and surrounding oxygens range from 1.58 Å (apical) to 1.78–2.04 Å (basal oxygens). The distance to the next-nearest oxygen atom below the pyramid base is much larger – 2.78 Å [8]. In our earlier EXAFS studies, we determined the first and second coordination shell radii in V_2O_5, corresponding to V–O distances of 1.68 Å and 1.98 Å, respectively. Similar values were obtained for some glasses, namely $45Li_2O{\cdot}10V_2O_5{\cdot}45P_2O_5$ [9].

The absorption edge is due to dipole-allowed 1s–4p transitions of vanadium [7, 8]. The "waves" visible on the XAFS curve of crystalline V_2O_5 just above the absorption edge have been ascribed to the multiple scattering of photoelectrons [7].

The observed systematic shift of the pre-edge peak towards lower energies for lower V_2O_5 contents (Fig. 1) reflects changes in the relative occupancy of aliovalent V^{4+} and V^{5+} states. For crystalline V_2O_5, where most of the vanadium atoms are in the V^{5+} state, the pre-peak is centred at 5467.6 eV, while for the glass $45Li_2O{\cdot}10V_2O_5{\cdot}45P_2O_5$, in which a considerable part of vanadium has V^{4+} valence due to the action of the modifier, its position is shifted to 5466.6 eV. Moreover, in the latter case the peak has a complex structure, which can be represented by a sum of two Gaussian maxima centred at 5466.6 and 5467.6 eV. The magnitudes of these component peaks reflect the occupancy of V^{4+} and V^{5+} states, respectively. By performing a best-fit deconvolution of the pre-edge peaks into their Gaussian components, it was possible to estimate the relative shares of vanadium in V^{5+} and V^{4+} states [11].

The absence or at least strong suppression of modulations just above the absorption edge observed for the studied glasses has been attributed to a relatively flat distribution of distances of neighbouring scattering atoms around vanadium in these complex amorphous systems.

The fact that the XANES spectra for lithium and silver glasses containing 15 mol % of the respective modifier (Fig. 2) are identical indicates that both modifiers (i.e. Li_2O and Ag_2O) act in the same way and introduce identical modifications to the local structure of vanadium. The absence of absorbance modulations above the edge of these glasses, contrasting with the clear oscillatory character of absorbance for crystalline V_2O_5, points to a disorder in the local structure of the former and precludes multiple scattering. This disorder in the local structure originates in part from the multitude of nearest-neighbour configurations in vanadate-phosphate glasses due to the mixed valence of vanadium, the presence of mixed vanadium-phosphate structural units, or broken V-O bonds.

When the amount of modifier is higher (35 mol %), one observes differences between the spectra of silver and lithium glasses in the XANES range. A shift of the

pre-edge peak to lower energies for the silver glass indicates an increase of the relative share of vanadium in the V^{4+} state. The presence of some structure in the XANES curve for $35Ag_2O{\cdot}30V_2O_5{\cdot}35P_2O_5$ just above the absorption edge (Fig. 3) suggests that the structural disorder in these glasses is smaller that of their lithium analogues. In particular, this may mean that the relative distances between absorbing and scattering atoms are better defined (or less distributed) in silver- than in lithium glasses.

5. Conclusions

It has been shown that XANES spectroscopy gives information on the population of aliovalent states of vanadium in glasses of the $Li_2O–V_2O_5–P_2O_5$ and $Ag_2O–V_2O_5–P_2O_5$ systems. An increase in modifier content leads to an increase of the number of vanadium atoms in the V^{4+} charge state. It has also been demonstrated that silver- and lithium glasses containing 15% of the respective modifier (Ag_2O or Li_2O) have very similar local structures. At higher contents (35%), however, there are discernible differences between the XANES curves for both glasses.

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