EXAFS/XANES Studies of the Local Structure of Amorphous Ionic and Electronic-Ionic Conductors

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Abstract

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 to study local structure of many solids and liquids. Their use is particularly valuable in case of amorphous systems where, 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. A special merit of the latter studies is that their results help to reveal the short-range structure of these conductors which is an important factor determining their transport properties.

This paper reports recent results of EXAFS/XANES studies of the local structure of selected electrically conducting glasses of the Li_2O-V_2O_5-P_2O_5 system and their silver analogs. All spectra were acquired at the K-edge of vanadium.

Keywords

EXAFS; XANES; amorphous ionic conductors; local structure; vanadate glasses;

Introduction

During over thirty years of progress in the field of solid state ionics it has been established that the transport of ions or both ions and electrons in electrically conducting solids is strongly dependent on the structure of the conducting materials (cf. a recent review by Hull

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[1]). Structural studies are relatively straightforward in the case of crystalline materials where one can apply a 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 the use of XRD much less efficient. There are however several spectroscopic methods, like e.g.: Raman scattering, infrared absorption (IR), or electron paramagnetic resonance (EPR) which can provide information on the local structure of these solids.

An important group of such methods are those of *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. Main advantages of the methods, compared to other spectroscopies are: i) their selectivity (they probe the vicinity of a given central atom that absorbs the X-rays up to a few Å); ii) insensitivity to long-range order, iii) possibility to determine basic parameters of several closest coordination shells (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 formal state of oxidation of transition metal atoms, symmetry of the cage formed around the central absorbing atom by its nearest neighbors, details on atomic or molecular orbitals, allowed or 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 [7-9].

In this paper we present results of our XANES studies on lithium vanadate-phosphate

glasses, which are known as mixed electronic-ionic conductors (cf. e.g. Ref. [10]), and their analogs with lithium replaced by silver.

Experimental

Lithium and silver vanadate and vanadate-phosphate glasses were prepared by a standard press-quenching technique [10] from dried reagent-grade chemicals such as: $AgNO_3$ (POCh), $LiNO_3$ (Aldrich), V_2O_5 (ABCR), $NH_4H_2PO_4$ (POCh). The composition of the series of lithium-containing glasses was described by the general formula $xLi_2O\cdot(100-2x)V_2O_5\cdot xP_2O_5$, where x=15, 35 and 45. Silver glasses had composition described by analogous formula, namely $xAg_2O\cdot(100-2x)V_2O_5\cdot xP_2O_5$, 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 A1 station at 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 Si (111) monochromator set either in a standard 2-crystal mode or a in 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 ionization chambers as detectors of incident and transmitted radiation.

Results

Lithium vanadate phosphate glasses

The XAFS spectra of glasses of composition $x Li_2O \cdot (100-2x) V_2O_5 \cdot x P_2O_5$ contain several characteristic features: a strong pre-peak, an absorption edge and oscillatory part above the edge. The absorbance modulations are stronger close to the edge and are damped at higher energies. Fast decay of oscillations of EXAFS signal observed for most glasses under study led to difficulties in obtaining reliable values of interatomic distances of secondary and farther 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 have focused on presentation of the results of the absorption spectra in the XANES region, i.e. approximately in the 5460-5540 eV range.

Fig.1 shows the XANES region of the spectra of the lithium vanadate-phosphate glasses under study. As the amount of V_2O_5 increases, several changes are observed: i) the prepeak 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 V_2O_5, are absent in the case of the investigated glasses.

Lithium vs. silver vanadate-phosphate glasses

In Fig.2 there are presented XANES spectra for a glass $15Li_2O \cdot 70V_2O_5 \cdot 15P_2O_5$, its silver analog $15Ag_2O \cdot 70V_2O_5 \cdot 15P_2O_5$ and a reference sample – crystalline V_2O_5. The spectra of both glasses are identical. The prepeak has in both cases 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 where there are well visible oscillations in this range.

The differences between spectra obtained for lithium- and silver glasses appear when the amount of a modifier is higher (35% mol) (Fig.3). The position of pre-edge peak of the

$35Ag_2O{\cdot}30V_2O_5{\cdot}35P_2O_5$ glass is shifted towards lower energies compared to its lithium analog. Additionally there are weak but discernible oscillations above the absorption edge for the silver glass, while for the lithium glass one observes a plateau.

Discussion

A strong pre-edge peak visible in all spectra in Fig.1 is due to a 1s-3d electronic transition in vanadium atom [7]. This transition is forbidden as long as a vanadium atom is in the 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 a central vanadium atom and surrounding oxygens are from 1.58 Å (apical) to 1.78-2.04Å (basal oxygens). The distance to the next-nearest oxygen atom below the pyramid base is much larger - 2.78Å [8]. In our earlier EXAFS studies we determined the 1st and 2nd coordination shell radius in V_2O_5, corresponding to V-O distances to 1.68 Å and 1.98Å respectively. Similar values were obtained for some glasses, namely $45Li_2O{\cdot}10V_2O_5{\cdot}45P_2O_5$ [11].

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

The observed systematic shift of the pre-edge peak towards lower energies for lower contents of V_2O_5 (Fig.1) reflects changes of relative occupancy of aliovalent V^{4+} and V^{5+} states. For crystalline V_2O_5, where most of vanadium are in the V^{5+} state, the pre-peak is centered at 5467.6 eV, while for a glass $45Li_2O{\cdot}10V_2O_5{\cdot}45P_2O_5$, when due to action of the modifier a considerable part of vanadium has V^{4+} valence, 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 centered 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 the 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 glasses under study have been attributed to a relatively flat distribution of distances of neighbor 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 around vanadium. The absence of absorbance modulations above the edge of these glasses, contrasting with clear oscillatory character of absorbance for crystalline V_2O_5, points to disorder in local structure of the former which precludes presence of effect of multiple scattering. That disorder in the local structure originates in part from the multitude of nearest-neighbor configurations in the vanadate-phosphate glasses due to e.g. mixed valence of vanadium, presence of mixed vanadium-phosphate structural units or broken V-O bonds.

When the amount of a modifier is higher (35 % mol) one observes differences between spectra for silver and lithium glasses in the XANES range. A shift of the pre-edge peak of the silver glass to lower energies indicates an increase of the relative share of vanadium in V^{4+} state. The presence of some structure of 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 less than in the case of their lithium analogs. In particular it may mean that the relative distances between absorbing and scattering atoms are better defined (or less distributed) in silver- than in lithium- glasses.

Conclusions

It has been shown that the 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 AgI-Ag_2O-V_2O_5 systems. The increase of the modifier content, leads to increase of number of vanadium atoms in the V^{4+} charge state. It has been also demonstrated that silver- and lithium glasses containing 15% of the respective modifier (Ag_2O or Li_2O) have very similar local structure. At higher contents (35%) however there are discernible differences between XANES curves for both glasses.

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Figure captions

Fig.1. XANES spectra of glasses of composition $x Li_2O \cdot (100-2x) V_2O_5 \cdot x P_2O_5$, where x=15, 35, 45, taken at K-edge of vanadium. Number next to curves denote the molar content of V_2O_5. A vertical line at pre-edge peak serves to emphasize position shifts.

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

Fig.3. XANES spectra of glasses of composition $35Li_2O \cdot 30V_2O_5 \cdot 35P_2O_5$ and $35Ag_2O \cdot 30V_2O_5 \cdot 35P_2O_5$, and of crystalline V_2O_5.

Figures

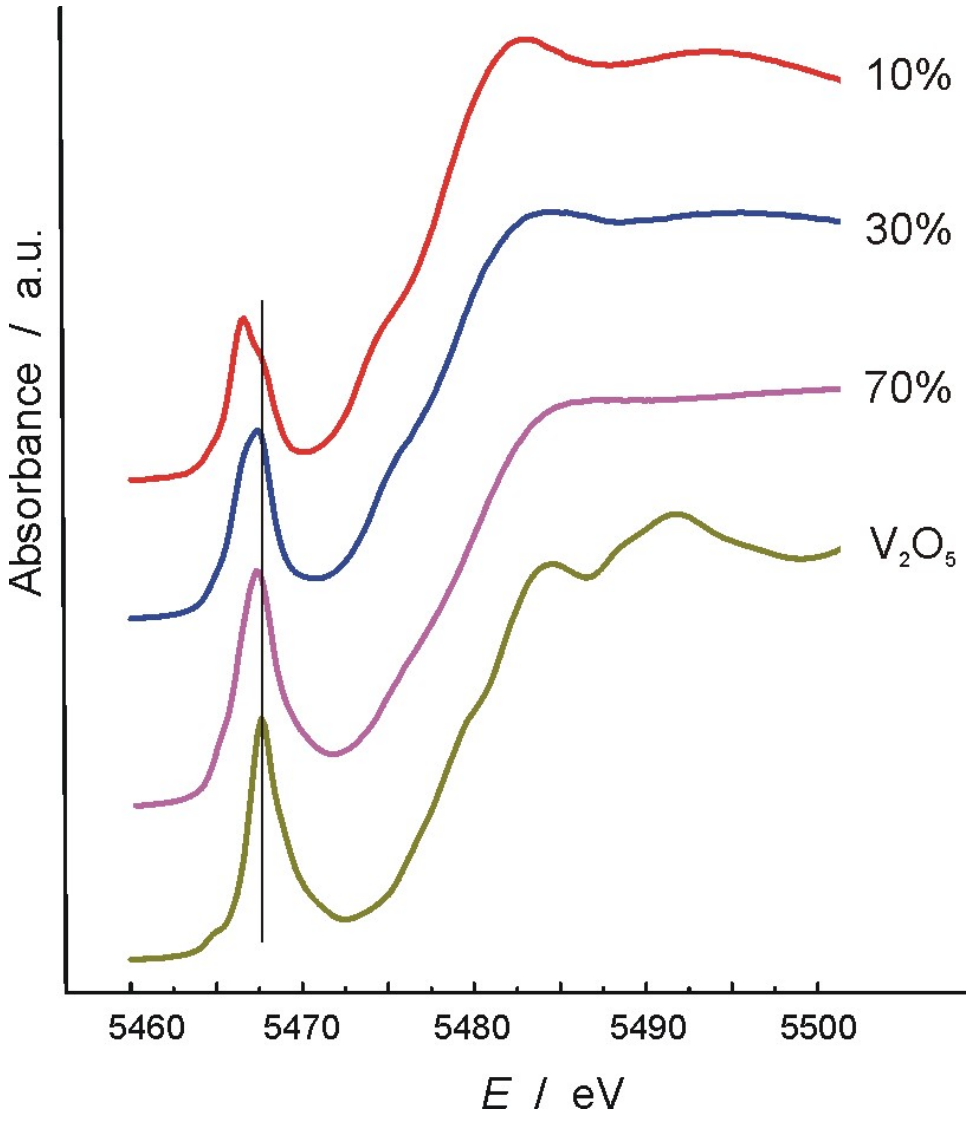

Fig.1. M.Wasiucionek *et al.*

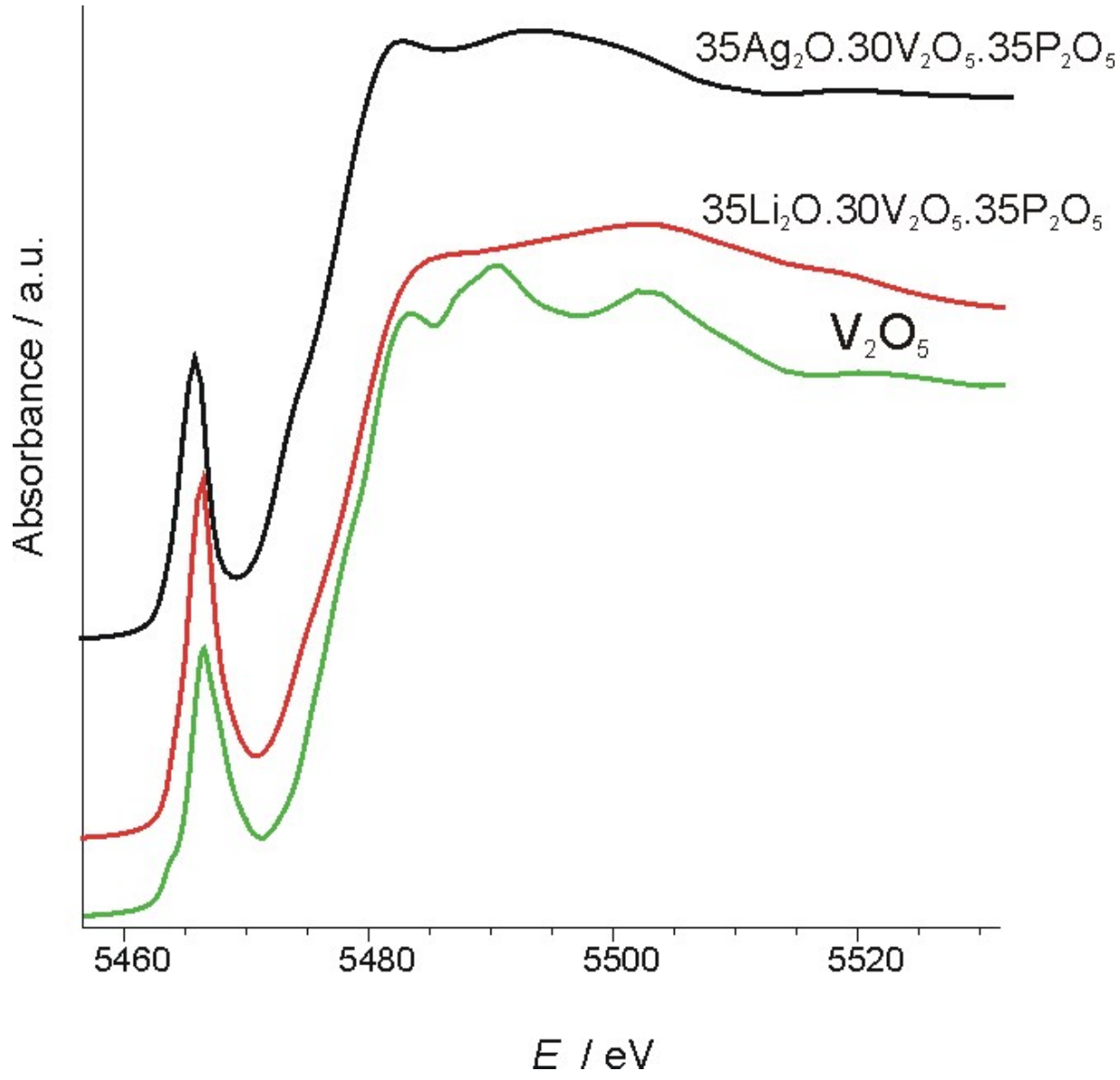

Fig.2. M.Wasiucionek *et al.*

Fig.3. Wasiucionek et al.