

**STUDY OF LOCAL ENVIRONMENT AROUND TUNGSTEN IN MIXED
VALENCE BARIUM-TUNGSTEN-PHOSPHATE GLASSES BY X-RAY
ABSORPTION SPECTROSCOPY**

A. Balerna, E. Bernieri, E. Burattini

Laboratori Nazionali di Frascati, Istituto Nazionale di Fisica Nucleare, C.P.13-00044 Frascati
(Roma), Italy

A. Kuzmin, J. Purans

Institute of Solid State Physics, University of Latvia, 226063 Riga, 8 Kengaraga st., Latvia

ABSTRACT

The XANES and the EXAFS of the L_1 - and L_3 - edges of tungsten in $BaO-P_2O_5-WO_3$ glasses and amorphous thin films $a-WO_3$ were studied using synchrotron radiation. The sets of distances were obtained in the first and the second coordination spheres of tungsten by a least square technique. It was found, that in all glasses tungsten atoms have strongly distorted oxygen octahedra, which are joined by vertices.

1. - INTRODUCTION

The use of high intensity synchrotron radiation allows to measure the X-ray absorption spectra using wide energy ranges and with high resolution, that leads the decrease of correlation effects between obtained structural parameters and increases the accuracy of their determination. Such "high resolution" X-ray absorption spectroscopy is a useful tool in the study of the local structure and electronic properties of different non-crystalline compounds.

The amorphous tungsten oxide thin films and glasses are potential materials for electro-optical applications due to their electrochromical properties, owing to the ability of tungsten to take a mixed valence. This paper is devoted to the interpretation of the L-edges absorption

spectra of tungsten in barium–tungsten–phosphate glasses with different content of tungsten oxide in comparison with our previous results for amorphous thin films (a-WO₃) and disordered crystals (c-WO_{3-x}) [1–3]. The quantitative analysis of the EXAFS spectra and the qualitative analysis of the XANES spectra are given. Some correlations between the valence of tungsten and the local structure of glasses were found.

2. – EXPERIMENT AND DATA ANALYSIS

X–ray absorption spectra of the tungsten L₁– and L₃– edges were recorded at the room temperature at the "ADONE" storage ring on the "PWA" BX–1 wiggler beamline . The storage ring "ADONE" operated at 20–50 mA and 1.5 GeV with the wiggler current 4000 A. The Si[220] channel–cut crystal monochromator was used, and the energy resolution was about 1 eV. The experimental spectra were measured in the ranges (12.050 ÷ 12.200) KeV for the L₁– edge and (10.050 ÷ 11.198)KeV for the L₃– edge. The samples were prepared at the Institute of Solid State Physics in Riga. The tungsten phosphate glasses had the following compositions in mol. %: 40BaO·40P₂O₅·20WO₃, 30BaO·30P₂O₅·40WO₃ and 20BaO·20P₂O₅·60WO₃ . The amorphous thin film (a-WO₃) was obtained by slow thermal evaporation in medium vacuum on a polyimide at substrate temperature T_S=200°C. The monoclinic tungsten oxide c-WO₃ and c-CaWO₄ were taken as reference compounds.

The data analysis was carried out according to a standard procedure [4]. The EXAFS spectra ($\chi(k)$) were calculated in the single scattering approximation using the expression :

$$\chi(k) = \sum_i \frac{N_i S_{0i}^2}{k R_i^2} f_i(\pi, k) \exp\left(-2 \sigma_i^2 k^2 - 2 \frac{R_i}{\lambda(k)}\right) \sin\left(2 k R_i + \phi_i(\pi, k) + \phi_c^l(k)\right),$$

where N_i is the coordination number, R_i is the interatomic distance, S_{0i}² is the multielectronic factor (used as a scaling factor), σ_i is the Debye – Waller factor, $f_i(\pi, k)$ and $\phi_i(\pi, k)$ are the backscattering amplitude and phase functions, $\phi_c^l(k)$ is the central atom (tungsten) phase shift, $\lambda=k/\Gamma$ is the electron mean free path. Theoretical amplitudes and phase shifts calculated in the spherical wave approximation by McKale et al. [5] have been used to fit spectra by a modified Levenberg – Marquardt method [6].

3. – RESULTS AND DISCUSSION

The EXAFS spectra $\chi(k)k^2$ ($k=2.0\div 15.0$ Å⁻¹) and their Fourier transforms (FT) for the L₃–edge are shown on Figs. 1 and 2. The peaks in FT correspond, as in crystalline and amorphous oxides [1,2], to the first coordination sphere of tungsten (0.8÷2.2 Å), multiple scattering (MS) effects in the first coordination sphere (2.2÷3.2 Å) and the second coordination sphere of tungsten (3.2÷4.2 Å). The structural parameters for the first and the second coordination spheres are respectively in Tables I and II .

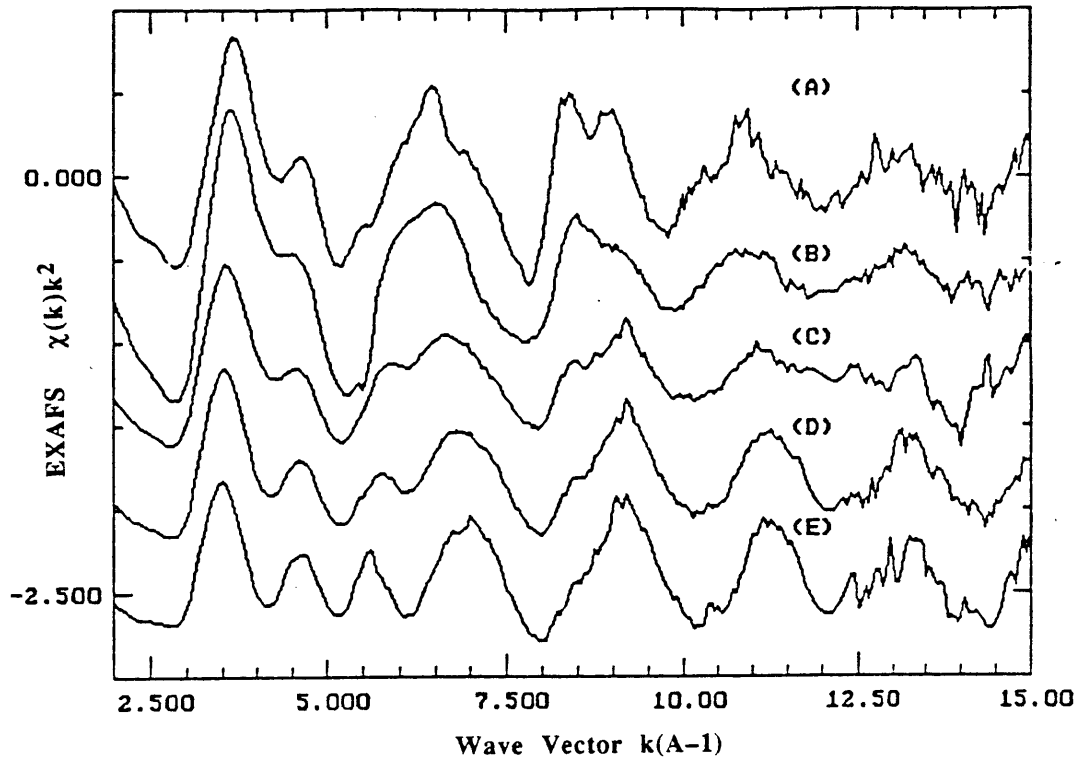


FIG. 1 - Experimental EXAFS-spectra $\chi(k)k^2$ for: (A) c- WO_3 , (B) a- WO_3 , (C) 60% WO_3 - glass, (D) 40% WO_3 - glass and (E) 20% WO_3 - glass.

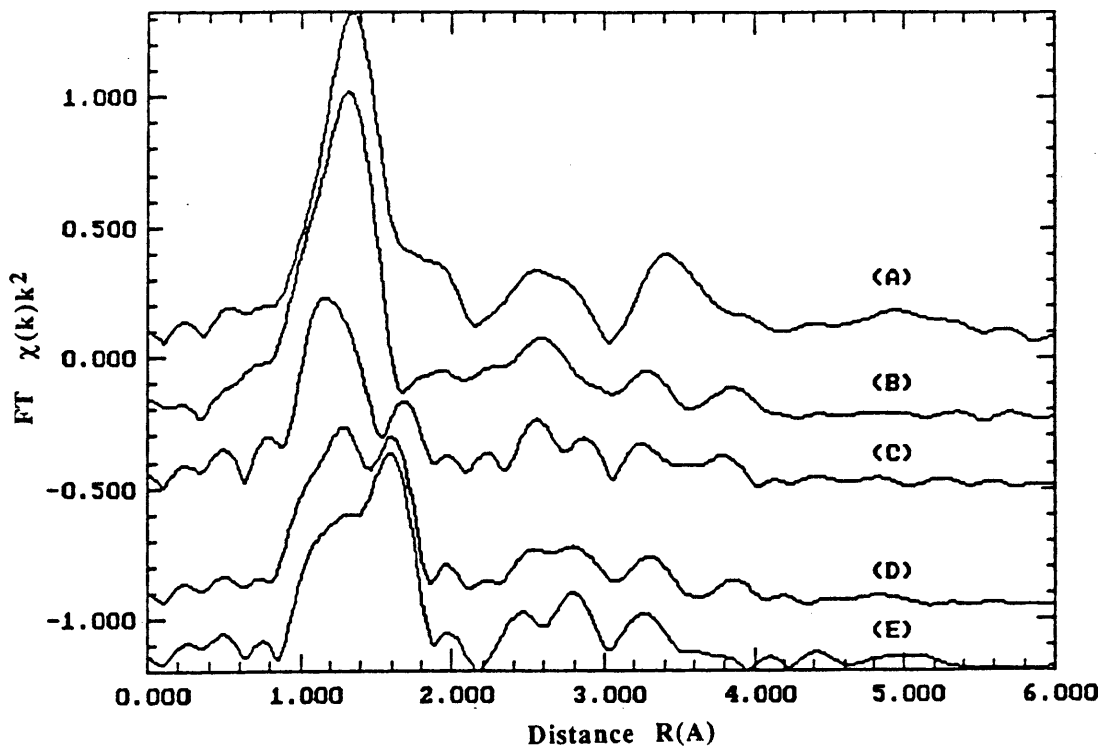


FIG. 2 - Fourier transforms of $\chi(k)k^2$ for: (A) c- WO_3 , (B) a- WO_3 , (C) 60% WO_3 - glass, (D) 40% WO_3 - glass and (E) 20% WO_3 - glass.

TABLE I – EXAFS parameters for the first coordination sphere of tungsten.

Compound	Bond	N	S_o^2	R, Å	$\sigma^2, \text{Å}^2$	$\Gamma, \text{Å}^2$
c-CaWO ₄	W-O	4	0.52	1.79	0.0010	0.40
c-WO ₃	W-O	2	0.50	1.75	0.0010	0.87
	W-O	2	0.50	1.80	0.0010	0.87
	W-O	1	0.50	1.90	0.0020	0.87
	W-O	2	0.50	2.12	0.0030	0.87
a-WO ₃	W-O	3.9	0.50	1.74	0.0050	0.54
	W-O	1.4	0.50	1.87	0.0020	0.54
	W-O	2.4	0.50	2.13	0.0070	0.54
60% WO ₃ -glass	W-O	2.4	0.50	1.72	0.0030	0.90
	W-O	2.2	0.50	1.84	0.0030	0.90
	W-O	2.4	0.50	2.01	0.0030	0.90
40% WO ₃ -glass	W-O	3.5	0.50	1.74	0.0020	0.88
	W-O	3.4	0.50	1.98	0.0030	0.88
	W-O	2.0	0.50	2.13	0.0030	0.88
20% WO ₃ -glass	W-O	3.7	0.50	1.73	0.0030	0.93
	W-O	2.9	0.50	1.96	0.0030	0.93
	W-O	3.6	0.50	2.09	0.0030	0.93

TABLE II – EXAFS parameters for the second coordination sphere of tungsten.

c-WO ₃	W-W	3.6	3.77	0.009	0.76
	W-O	10.2	4.10	0.030	0.60
60% WO ₃ -glass	W-W	1.4	3.73	0.009	0.60
	W-W	0.2	3.84	0.001	0.60
	W-O	12.0	4.14	0.050	0.60
40% WO ₃ -glass	W-W	0.9	3.73	0.005	0.57
	W-W	0.3	3.86	0.002	0.57
	W-O	12.3	4.12	0.049	0.57
20% WO ₃ -glass	W-W	0.3	3.66	0.002	0.46
	W-W	2.7	3.81	0.014	0.46
	W-O	12.4	4.10	0.048	0.46

The oxygen octahedra [WO₆] in glasses are strongly distorted that lead to the splitting of the first peak in the FT. Previously we observed the splitting of the first peak in the FT of crystalline and amorphous tungsten oxides [1,2]. Also Studer et. al. [7] observed earlier the splitting of the first peak in the FT on short (1.77 Å) and long (2.0 Å) distances in potassium-

tungsten-phosphate glasses. "High resolution" EXAFS measurements allowed to separate three main groups of distances W-O: the short (1.71 ± 1.74 Å), the middle (1.84 ± 1.96 Å) and the long (>2.0 Å). The average W-O and W-W distances change depending on the WO_3 concentration from 1.80 Å to 1.95 Å and from 3.70 Å to 3.80 Å, and are larger in the glass with smaller concentration of tungsten oxide. Our previous results [2] allow to attribute such monotonous changing with the presence of tungsten atoms, which have the 5+ valence.

The peak in the FT (2.2 ± 3.2 Å) corresponding to MS effects can be attributed to processes of scattering in near collinear chains such as O-W-O and W-O-W. The relatively large amplitude can be explained by the focusing influence of tungsten and oxygen atoms. The analysis of the multiple scattering effects in the first and the second shells is in progress.

Figures 3 and 4 show the XANES for the L_1 - and L_3 - edges of tungsten in glasses, amorphous thin film a- WO_3 and referenced compounds c- WO_3 and c- CaWO_4 . The local environment of tungsten in c- WO_3 is a distorted oxygen octahedron and in c- CaWO_4 - a regular oxygen tetrahedron. The "white line" in the L_3 - spectrum originates from the allowed dipole transition $2p(\text{W}) \rightarrow 5d(\text{W})$. The variation of its amplitude relates with the occupancy of d states, their splitting in the field of the surrounding oxygens and changing of the average W-O distance.

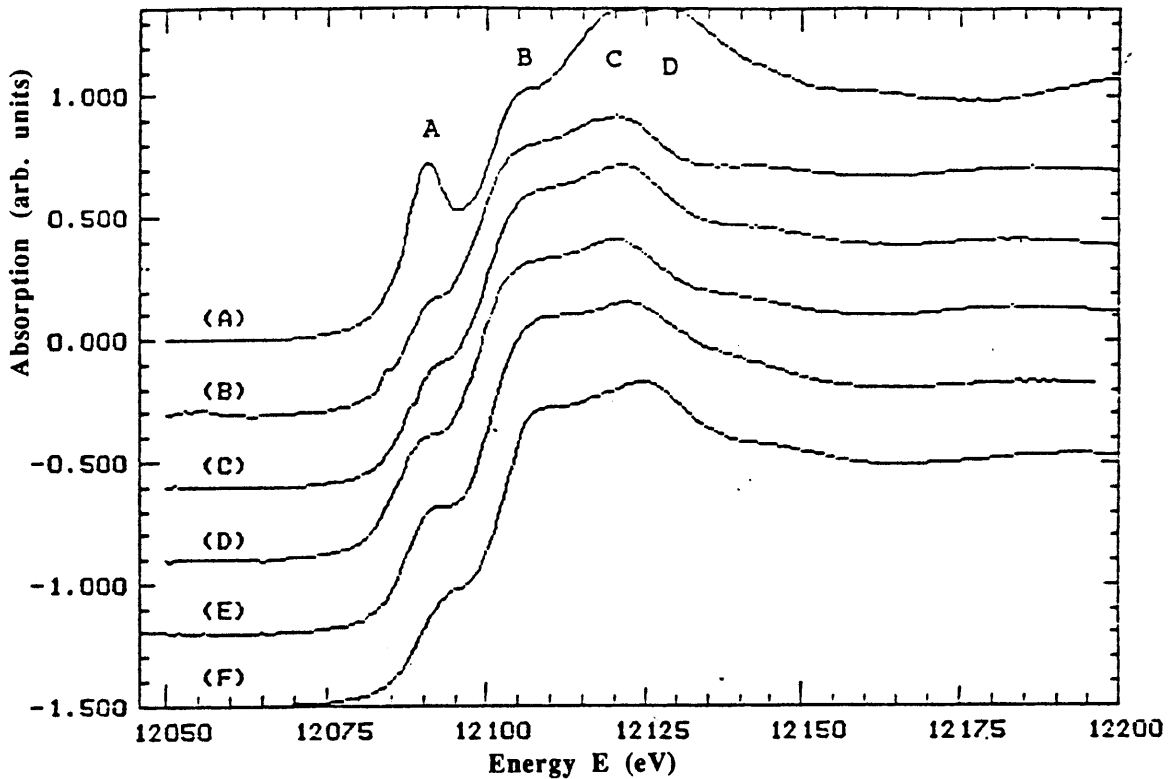


FIG. 3 - The XANES for L_1 -edge of tungsten in (A) c- CaWO_4 , (B) 20% WO_3 - glass, (C) 40% WO_3 -glass, (D) 60% WO_3 - glass, (E) a- WO_3 , (F) c- WO_3 .

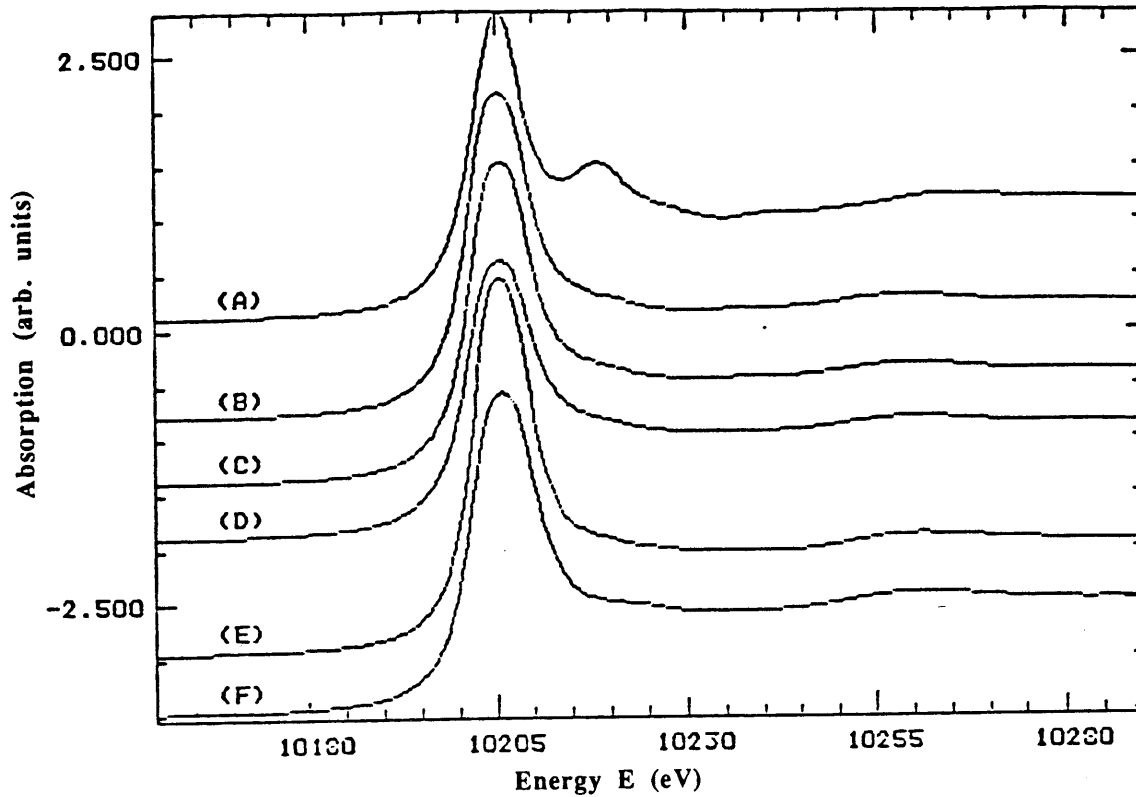


FIG. 4 - The XANES for L_3 -edge of tungsten in (A) c- CaWO_4 , (B) 20% WO_3 - glass, (C) 40% WO_3 -glass, (D) 60% WO_3 - glass, (E) a- WO_3 , (F) c- WO_3 .

The L_1 - edge has a complicated structure. The shoulder (A) placed on the edge corresponds to the forbidden dipole transition $2s(\text{W}) \rightarrow 5d(\text{W})$, which is allowed due to the mixing between the tungsten $5d$ state and $2p$ states of oxygen atoms and the absence of the inversion center and is related to the octahedra distortion. The main peak (B) is the allowed dipole transition $2s(\text{W}) \rightarrow 6p(\text{W})$. It is established, that the size of the shoulder depends strongly on the coordination number of tungsten and in all glasses corresponds to the distorted octahedral environment, that is in good agreement with data obtained from EXAFS spectra. The features (C, D) placed above the main peak beyond the absorption edge are conditioned by the scattering processes in the second coordination sphere. The XANES for the amorphous thin film a- WO_3 is similar to one for glasses, however, the shoulder in the case of a- WO_3 is more marked, that can be attributed to the larger distortion of the octahedra.

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