

XAFS Studies of Octahedral Amorphous Oxides

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The relationships between the structures of octahedral and tetrahedral amorphous oxides, studied by XAFS spectroscopy, are considered. It was found that α - WO_3 , α - MoO_3 , α - V_2O_5 thin films and glasses have strongly distorted, but well defined, oxygen octahedra, which are joined by vertices (α - WO_3 , α - MoO_3) or by vertices and edges (α - V_2O_5), and form a random network. At the same time, α - IrO_2 and α - NiO have less distorted oxygen octahedra, which form the rutile type and rock salt type nanocrystalline structures. The variation of the structure with the change of the metal valence is considered and the possibility of small radius polaron detection by XAFS is discussed.

KEYWORDS: WO_3 , MoO_3 , V_2O_5 , IrO_2 , NiO , structure, X-ray-absorption spectra

§1. Introduction

While the structures of classical amorphous oxides, like vitreous silica with regular oxygen tetrahedra SiO_4 , are comparatively well understood, the structures of octahedral amorphous oxides, like α - WO_3 , α - MoO_3 , α - V_2O_5 , α - IrO_2 and α - Ta_2O_5 , consisting of the distorted octahedra, remain elusive.^{1,2)} In complex amorphous oxides, like mixed-valence transition metal oxides, there may be more than one structural unit, and the possibility of well defined combinations of basic structural units exists too.

In this work we present the relationships between the structures of octahedral and tetrahedral amorphous oxides studied by XAFS spectroscopy. The new improved XAFS data with higher statistical accuracy are reported for several amorphous oxides.³⁻⁶⁾

§2. Experimental

The amorphous thin films were prepared by vacuum evaporation (α - WO_3 , α - MoO_3 and α - V_2O_5) and reactive sputtering (α - WO_3 , α - IrO_2 and α - NiO) on a polyimide substrate.³⁻⁵⁾ The tungsten ($\text{BaO-P}_2\text{O}_5\text{-WO}_3$) and ($\text{GeO}_2\text{-P}_2\text{O}_5\text{-V}_2\text{O}_5$) phosphate glasses were prepared by conventional techniques.^{4,6)} Transmission XAFS spectra were measured at W, Ir L_3 -edges and Mo, V, Ni K-edges at the ADONE storage ring (INFN LNF, Frascati) using the EXAFS station on the "PWA" wiggler beam line. The synchrotron radiation has been monochromatized using the Si(111) and Si(220) channel-cut crystal

monochromators, and its intensity has been measured by two ionization chambers filled with a krypton gas.

The data analysis was carried out for the first coordination shell according to the standard procedure in the spherical wave approximation.^{3,6)} The multiple-scattering (MS) effects in the first and the second shells were compared with *ab initio* calculations of several crystals.⁷⁾

§3. Results and Discussion

XAFS analysis of the results for octahedral amorphous oxides has some specific features. In Figs. 1-4 the Fourier transforms (FT) of the experimental EXAFS $\chi(k)k^2$ signals for amorphous and crystalline WO_3 , MoO_3 , V_2O_5 and NiO are shown. The Me-O distances in the first shell of α - WO_3 , α - MoO_3 and α - V_2O_5 vary in a wide range from 1.6 to 2.3 Å.³⁻⁸⁾ These distances correspond to three subshells: Me=O₁ - terminal oxygen, Me-O₂-Me - bridging oxygen, Me-O₃ - next nonbridging oxygen. The distortion of octahedra increases in the series α - WO_3 , α - MoO_3 , α - V_2O_5 . Also for amorphous α - Ta_2O_5 and α - Nb_2O_5 , it was found the wide distribution of Me-O distances. In contradiction, tetrahedral materials show very small variation of distances being 3.0 % for amorphous Ge and 2.8 % for vitreous silica.¹⁾

The MS effects in the first shell were simulated for isolated octahedra WO_6 with different *off-center* position of tungsten. For the second shell the W-O-W chain with angles in the interval from 90 to 180 degree was used as a model to estimate the MS contribution.

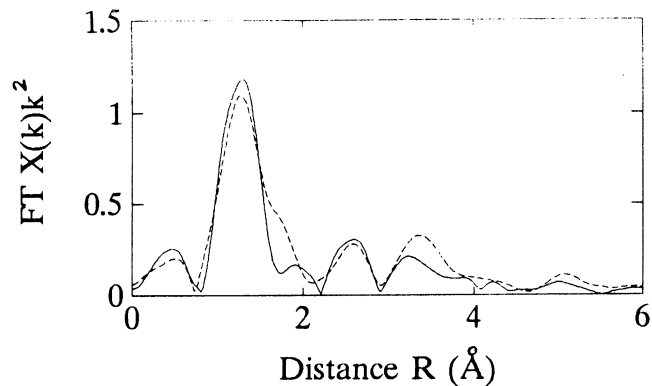


Fig. 1. Fourier transforms of the W L_3 -edge EXAFS $\chi(k)k^2$. Solid line - amorphous a-WO₃, dashed line - monoclinic m-WO₃.

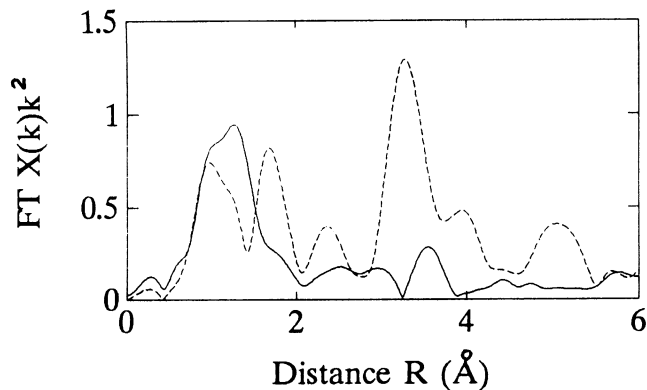


Fig. 2. Fourier transforms of the Mo K -edge EXAFS $\chi(k)k^2$. Solid line - amorphous a-MoO₃, dashed line - crystalline c-MoO₃.

In perovskite like amorphous and crystalline WO₃ and MoO₃, the peaks in FT between 2.2 and 3.2 Å (Figs. 1-2) can be attributed to MS processes in the first shell with partial contribution from the double-peak structure of the second shell, which is typical for heavy elements. The peaks between 3.2 and 4.2 Å are due to MS processes in the nearly collinear chains in the second shell and contribution of oxygen atoms located in the third shell. The intensity of the last peak is very sensitive to the value of the Me-O-Me angle. At the same time, in rutile type IrO₂ and rock salt type NiO the MS effects are smaller and the peaks in FT correspond well to ones in crystalline materials.⁷⁾ Thus, we conclude that a-WO₃ and a-MoO₃ thin films and glasses have strongly distorted, but well defined, oxygen octahedra, which are joined by vertices (a-WO₃, a-MoO₃) or by vertices and edges (a-V₂O₅), and form a random network.

In contradiction with classical tetrahedral oxides (SiO₂ and GeO₂), the octahedral transition metal oxides in crystalline and amorphous states have a wide range of oxidation states of the metal ion. In tungsten compounds WO_{3-x} with different valence state of tungsten

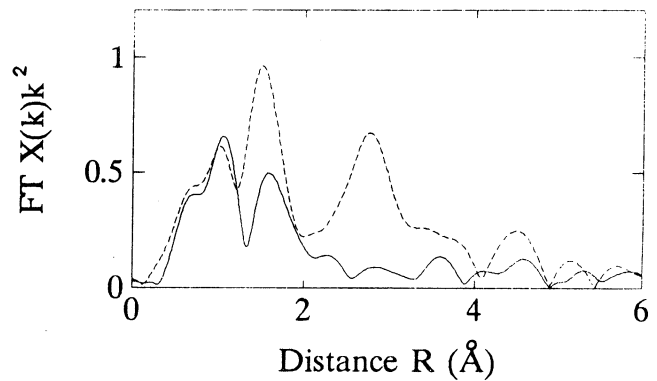


Fig. 3. Fourier transforms of the V K -edge EXAFS $\chi(k)k^2$. Solid line - amorphous a-V₂O₅, dashed line - crystalline c-V₂O₅.

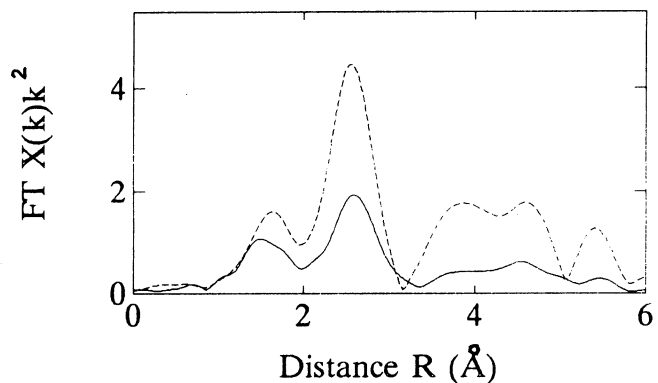


Fig. 4. Fourier transforms of the Ni K -edge EXAFS $\chi(k)k^2$. Solid line - amorphous a-NiO, dashed line - crystalline c-NiO.

(from W⁴⁺ to W⁶⁺), we have observed a drastic change of the XAFS spectra and their FT.³⁾ The average W-O distance increases monotonically with a reduction of tungsten oxidation state and with a decrease of WO₆ octahedra distortion. The same effect was observed also in tungsten-phosphate glasses.⁷⁾ This results are in good agreement with known bond length - bond strength (valence) correlation for mixed-valence tungsten oxides.⁹⁾

In a-WO₃ thin films with prominent electrochromic properties, we have observed the increase of the two peaks amplitude in FT at 3.2 and 3.8 Å under the coloration and a small change of the middle distance W-O in the first shell that can be attributed to the change of the valence state of tungsten from W⁶⁺ to W⁵⁺.

It is known that strong electron-phonon coupling in non-stoichiometric WO_{3-x} leads to the formation of small radius polarons.¹⁰⁾ Also, tungsten, molybdenum and vanadium phosphate glasses are non-stoichiometric and the extra electrons being localized at the metal site resulting in the formation of reduced metal ions (W⁵⁺, Mo⁵⁺ or V⁴⁺).¹¹⁾ Strong interaction between unpaired electrons and the lattice leads to displacement of oxygens

around transition metal ions that correspond to change of bond distances and the degree of distortion of octahedra. Therefore, we suppose that observed by XAFS method structural changes in α - WO_3 thin films, glasses and WO_{3-x} crystals correspond to formation of small radius polaron in these materials.

§4. Summary and Conclusions

The wide set of distances (Me-O) in the first coordination shell and multiple-scattering effects in nearly linear chains O-Me-O and Me-O-Me are very important for interpretation of XAFS for amorphous octahedral oxides. The low-noise XAFS measurements and multishell fitting procedure allow to obtain the set of close lying distances in the first coordination shell with a high accuracy. The MS contributions in amorphous octahedral oxides α - WO_3 and α - MoO_3 are similar to one in perovskite-type ReO_3 and monoclinic WO_3 crystals.

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