

The Study of Local Structure in Silica-Titania Glass by XAFS

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Introduction

Silica-titania system is of significant technological importance, such as ultralow expansion glasses, antireflective thin films and catalytic materials.

The understanding of the structural characteristics of this binary material and the relationships with the physico-chemical properties plays an important role in a wide range of applied sciences [1].

In the present work we have used the X-ray Absorption in Fine Structure (XAFS) technique near the Ti K absorption edge to study local parameters of structure of the material in EXAFS (Extended X-ray Absorption Fine Structure) region and a feature analysis in XANES (X-ray Absorption Near Edge Structure) region.

Method

High purity silica-titania glasses with TiO₂ concentration in the range 4 – 11 wt. % were prepared by the flame aerosol technique at Laboratory of Photonic Materials & Devices (LIQC) – UNICAMP [2]. Initially, porous boules of fine oxide particles were produced by the flame hydrolysis and oxidation reaction of vapor-phase binary mixture of SiO₂ and TiO₂. SiCl₄ and TiCl₄ halides were used as precursors and O₂ was used as a carrier gas, as well as to control the TiO₂ concentrations. Afterwards, a consolidation process in an electric furnace was carried out at 1400 °C, resulting in a sintered and bubble-free preform.

The Ti K-edge spectra were recorded in transmission mode at room temperature using the XAFS BL-9A beamline equipped with a Si(111) double-crystal monochromator.

Results and Discussion

The analysis in XANES spectra of the standard sample (rutile TiO₂) showed three low intensity pre-edge peaks, characteristic of a typical octahedral Ti sites. The intensity of a narrow pre-edge peak at 4968.6 eV increases when the TiO₂ concentration decreases, but no change in the energy position was noticed (Figure 1). These pre-edge features suggest the Ti⁴⁺ valence for all samples [3].

In Figure 2 an interesting aspect was observed in the Fourier transform magnitudes, smaller for higher TiO₂ concentration samples. This result is probably related to the existence of both 1.8 Å and 2.0 Å different Ti–O bonds lengths that correspond to the mixture of tetrahedral and octahedral sites for samples with higher TiO₂ concentrations, giving rise to a destructive interference of sinusoids in the Fourier transforms [4].

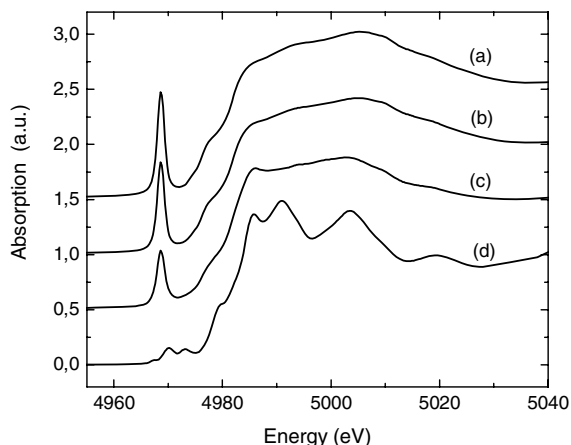


Figure 1. The Ti K-edge XANES spectra of SiO₂–TiO₂: (a) sample with 4 wt. % in TiO₂; (b) 6.5 wt. %; (c) 11 wt. %; and (d) rutile TiO₂.

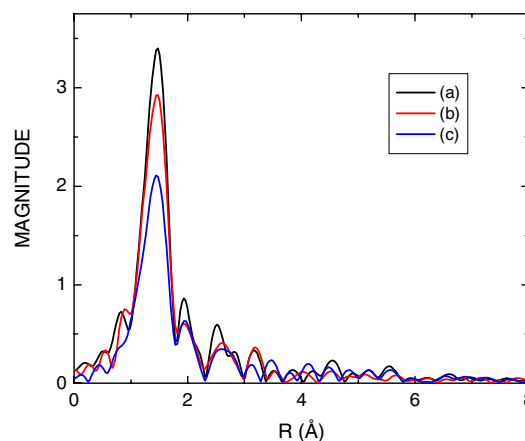


Figure 2. Fourier transforms of (a) sample with 4 wt. % in TiO₂; (b) 6.5 wt. %; and (c) 11 wt. %.

References

- [1] X. Gao et al., *Catalysis Today*, 51, 233 (1999).
- [2] J. S. dos Santos et al., *Rev. Sci. Instrum.*, 77, 055106 (2006).
- [3] G. A. Waychunas, *Am. Mineral.*, 72, 89 (1987).
- [4] R. B. Gregor et al., *J. Non-Cryst. Solids*, 55, 27 (1983).

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