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EXAFS Study of SnO₂ Xerogel Doped with Sb and PTCDAJ. Padežnik Gomilšek^{1,*}, U. Lavrenčič Štangar^{2,3}, A. Šurca Vuk², G. Bratina³, I. Arčon^{3,4} and A. Kodre^{4,5}¹Faculty of Mechanical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia²National Institute of Chemistry, Hajdrihova 19, SI-1000, Ljubljana, Slovenia³Nova Gorica Polytechnics, Vipavska 13, SI-5000 Nova Gorica, Slovenia⁴J. Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia⁵Faculty of Mathematics and Physics, Jadranska 19, SI-1000 Ljubljana, Slovenia

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Abstract

SnO₂ and doped Sb:SnO₂ sol, prepared by a precipitation-peptization sol-gel process, has been used as a host for the incorporation of an organic semiconductor, the perylene dye (PTCDA). The structure of the SnO₂ gel host together with the effect of inorganic (Sb) and organic (PTCDA) doping is studied with EXAFS at the Sn and Sb K-edge. Distinct neighbor shells are resolved only up to 4 Å. The corresponding radii are the same as in a cassiterite crystal structure with a 60% reduction in the Sn neighbor population. In the spectra at the Sn edge, the doping with Sb and/or a small concentration of PTCDA produces no detectable effect. At higher content of PTCDA, however, the number of the first oxygen neighbors is diminished by ~30% indicating that the disordered organic groups from the dye molecule reach right into the Sn neighborhood. In the weaker Sb EXAFS spectra only the first shell of oxygen neighbors is resolved: again the static disorder is higher in the presence of the organic dopant.

1. Introduction

The sol-gel processing has been developed into an appropriate technique for producing inorganic and organic-inorganic glasslike materials [1]. Owing to mild processing conditions, organic molecules can be introduced into inorganic polymeric matrices. The inorganic matrix in this study is tin-oxide gel derived by alkaline aqueous sol-gel route [2]. For comparison, SnO₂ matrix was made also according to a peroxo route [3]. Pure or Sb-doped SnO₂ in thin film form is a promising material for transparent conductive electrodes, ion-storage electrodes or low-emitting coatings for advanced glazings [3–8].

In addition to inorganic doping, perylene tetracarboxylic acid dianhydride (PTCDA) as an organic semiconductor with attractive optical properties has also been introduced into the SnO₂ gel matrix. Generally, the photochemical and mechanical stability of the dye is increased by using inorganic host systems [9, 10]. PTCDA is highly insoluble in common solvents used for sol-gel synthesis (alcohol, water) so that a homogeneous dispersion in the sol-gel host is not easy to achieve. However, good solubility and distribution of perylene derivatives was found in alkaline medium of SnO₂ sol that was prepared by the aqueous precipitation-peptization sol-gel process.

From the structural point of view, SnO₂ can serve as an insertion compound (to be used for example as an optically passive counter electrode in electrochromic devices) since it has the rutile structure with existing tunnels expanding along the 001 direction, which enable the intercalation/deintercalation of small ions (Li⁺) through the thin film. The ion-insertion properties can

be additionally improved by: (i) decreasing electronic resistivity and the particle grain size with doping; and (ii) increasing the porosity and the number of redox centres [7]. The induced disorder of the rutile structure through doping can be investigated by EXAFS. Thus, EXAFS of various SnO₂ xerogel samples is used to study the structural environment around tin atom and the disordering effect of Sb and PTCDA guest species.

2. Synthesis

SnO₂ aqueous sol (*a*) was made according to ref. [2] from SnCl₄·5H₂O precursor (Table I). Doping with Sb was achieved by adding SbCl₃ (7 mol% vs. Sn) in the initial aqueous solution acidified with HCl to dissolve Sb-salt. A precipitate was formed with the addition of ammonia up to pH 3. After repeated washing with water the precipitate was peptised with 8 mL of concentrated aqueous ammonia, which resulted in a basic aqueous sol (pH ~ 10). To this sol (undoped and Sb-doped) various amounts of PTCDA (0.5–5 mol%), previously dissolved in 9% KOH, were introduced. The gelling time of the sol in a closed vessel was a few days at room temperature.

SnO₂ peroxo sol (*p*) was made for comparison purposes according to ref. [3]. Conc. H₂O₂ was added dropwise to SnCl₂·2H₂O precursor leading to the strong exothermic reaction. The formed solution was evaporated at 70 °C to get a viscous opaque gel, which was diluted with ethanol. To this sol a small amount of bis end-capped triethoxysilane with a covalently linked mid polyether chain (ICS-PPG4000 [11], 1 mol%) was added to enhance the porosity of the oxide samples in order to improve ion-storage characteristics.

Xerogel powders were made from gels by drying them at ambient conditions.

Table I. List of SnO₂ xerogel samples (labels: *a* – inorganic from aqueous route, *p* – hybrid organic-inorganic from peroxo route, *Sb* – Sb doped, *P_l* – low concentration of PTCDA, *P_h* – high concentration of PTCDA).

label	route	Sb	PTCDA
a	aqueous		
aSb	aqueous	7 mol% vs. Sn	
aP _l	aqueous		0.5 mol.%
aSbP _l	aqueous	7 mol% vs. Sn	0.5 mol.%
aP _h	aqueous		5 mol.%
p	peroxo		

*E-mail: jana.padeznik@uni-mb.si

3. Experiment

Samples of xerogel powders were prepared on multiple layers of adhesive tape to gain sufficient absorption jump: 0.2–0.6 at Sn K edge (29200 eV) and ~0.2 at Sb K edge (30491 eV). Standard Sn and Sb K-edge EXAFS spectra were measured at the X1 station of HASYLAB synchrotron facility at DESY (Hamburg, Germany) using a two-crystal Si 311 monochromator with energy resolution of about 6 eV. Owing to the high photon energy, the incident beam is free of harmonic contamination. The energy scale at Sn edge was calibrated by a simultaneous absorption measurement of a thin Sn foil, while at Sb edge only the stability of the monochromator scale was monitoring by a simultaneous measurement of both Sb doped samples. Spectra were analysed by FEFF6 code [12, 13].

4. Results

The XANES spectra of all samples are very similar showing no detectable valence shift.

By EXAFS, the structure of pure inorganic SnO₂ gel host derived from aqueous sol (*a*) is compared to that of hybrid organic-inorganic xerogel made by peroxo sol-gel route (*p*). In both *r*-space spectra, a coherent signal is found only up to *r* ~ 4 Å indicating a short-range order. Obviously, the preparation route influences the local structure: a sharp first peak observed in the *a* spectrum is split into two smaller peaks in the *p* spectrum (Fig. 1).

For *a* spectrum, a very good fit of the first peak can be obtained with a model of 6 oxygen neighbors at 2.06 Å as in the cassiterite crystal [14]. With two subsequent shells of Sn neighbors the entire *a* spectrum is roughly described: the distances agree with crystal data but the occupation number is reduced to ~40% due to disorder in the structure (Table II). The signal of farther oxygen neighbors in the cassiterite structure is small and their parameters cannot be reliably extracted from the xerogel data.

The nearest neighborhood of Sn in the hybrid organic-inorganic xerogel can be modeled with a combined model of a reduced number (~4.5) of oxygen atoms at distances as in the cassiterite structure and of approximately 1.5 chlorine atoms at 2.40 Å as in a SnCl₄ structure [15]. Thus, a relatively large fraction of Sn atoms in the xerogel made by peroxo route remains as chloride while in the xerogel made by aqueous precipitation-peptization route no Sn-Cl bonds are detected, confirming that Cl from starting materials is efficiently washed out.

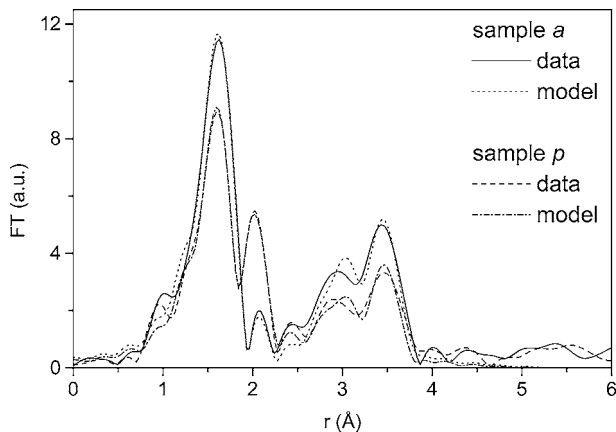


Fig. 1. Fourier transform of the Sn K edge EXAFS of the SnO₂ xerogel and its 3-path model in comparison with SnO₂ xerogel made by peroxo route and its 4-path model (*k*³-weighted, 3–14 Å⁻¹).

Table II. Model parameters for spectra at Sn K edge, *k* range 3–14 Å⁻¹, *r* range 1.3–4 Å (except for sample *aP_h*: 1.3–2.1), *k*³-weighted, the numbers in parentheses indicate uncertainties of the last digit, for sample *a* the coordination number *N*₁ was kept fixed.

	SnO ₂ crystal	sample <i>a</i>	sample <i>p</i>	sample <i>aP_h</i>
<i>r</i> _{fit}	–	0.008	0.009	0.006
<i>N</i> ₁ (O)	6	6	4.6(5)	4.2(4)
<i>r</i> ₁ [Å]	2.05	2.06(1)	2.06(1)	2.06(1)
<i>σ</i> ₁ ² [Å ²]	–	0.004(1)	0.005(1)	0.003(1)
<i>N</i> ₂ (Sn)	2	0.9(1)	0.6(4)	–
<i>r</i> ₂ [Å]	3.19	3.22(1)	3.22(1)	–
<i>σ</i> ₂ ² [Å ²]	–	0.002(1)	0.003(1)	–
<i>N</i> ₃ (O)	4	–	–	–
<i>r</i> ₃ [Å]	3.59	–	–	–
<i>N</i> ₄ (Sn)	8	3.1(9)	3.0(10)	–
<i>r</i> ₄ [Å]	3.71	3.74(7)	3.74(1)	–
<i>σ</i> ₄ ² [Å ²]	–	0.005(1)	0.006(2)	–
<i>N</i> ₅ (Cl)	–	–	1.5(1)	–
<i>r</i> ₅ [Å]	–	–	2.41(1)	–
<i>σ</i> ₅ ² [Å ²]	–	–	0.002(1)	–

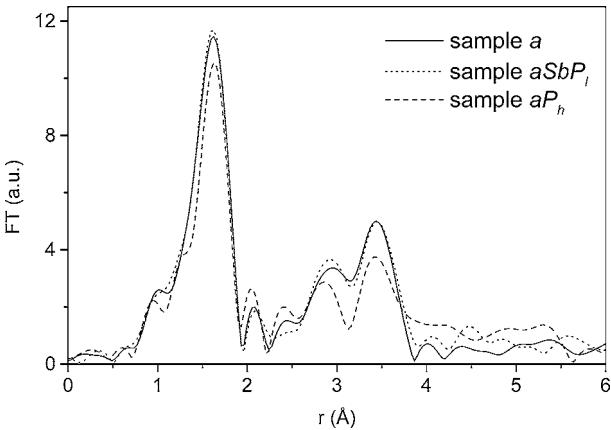


Fig. 2. The effect of doping the SnO₂ xerogel with Sb and low concentration of PTCDA in comparison with doping with high concentration of PTCDA (*k*³-weighted, 3–14 Å⁻¹).

It can be seen from Fig. 2 that doping with Sb (7 mol% vs. Sn) and a small concentration of PTCDA (0.5 mol%) produces no detectable effect in the spectra at the Sn edge. Doping with high concentration of PTCDA (5 mol%), however, results in a lower signal of the first neighbors. A single-shell model differs from that of the *a* spectrum only in a lower occupation number while the distance and the Debye-Waller factor remain practically the same. The missing oxygen neighbors are not replaced with another species indicating that the disordered organic groups from the dye reach right into the Sn neighborhood.

The spectra at Sb K edge exhibit a higher level of noise due to the relatively small concentration of Sb atoms and a strong background absorption limiting the scope of modeling. Nevertheless, some information can be extracted: both Fourier spectra exhibit only one prominent peak indicating highly disordered Sb-sites (Fig. 3). The first shell around Sb consists of ~5 oxygen atoms at ~1.95 Å. In Sb-doped xerogels, the additional doping with PTCDA even at low concentration results in higher static disorder around Sb atoms (Table III).

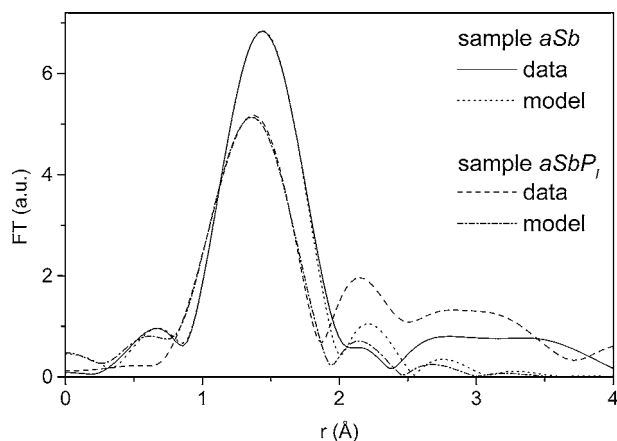


Fig. 3. Fourier transform of the Sb K edge EXAFS of the Sb-doped SnO₂ xerogel in comparison with Sb- and low concentration PTCDA-doped xerogel. Single-path models (k^3 -weighted, $2.7\text{--}9.1\text{ \AA}^{-1}$) are also shown.

Table III. Model parameters for spectra at the Sb K-edge, k range $2.7\text{--}9.1\text{ \AA}^{-1}$, r range $1.0\text{--}1.8\text{ \AA}$, k^3 -weighted, the numbers in parentheses indicate uncertainties of the last digit.

	sample aSb	sample aSbPi
r_{fit}	0.001	0.002
N_1 (O)	4.9(5)	5.0(8)
r_1 [Å]	1.98(1)	1.93(1)
σ_1^2 [Å ²]	0.003(1)	0.006(2)

5. Conclusions

Tin-oxide gel was doped with Sb and/or PTCDA to tailor the electrochemical and optical properties of the final material, keeping the host structure nearly unchanged with evenly dispersed dopant in it. Indeed, all Sn EXAFS spectra are adequately modeled

by the structure of SnO₂ cassiterite with reduced occupation numbers.

The disorder increases with the content of the organic dopant. Higher concentration induces a drop of the first neighbor signal indicating a homogeneous distribution of the organic dye.

Acknowledgements

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