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XAS study of murataite-based ceramics and crystalline film of ThO_2

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Sample preparation

Crystalline film ThO_2 sample was mounted under the synchrotron radiation beam, murataite ceramics sample was mixed with cellulose, ground and pressed into a pellet.

EXAFS spectroscopy

X-ray absorption spectra of the L_{III} absorption edge in the X-ray fluorescence yield registration mode (ThO_2 film) and in transmission mode (murataite ceramics) were measured at the station «Structural material science» of the Kurchatov Synchrotron Radiation Center of the National Research Center «Kurchatov Institute» [S1].

Synchrotron radiation was obtained using the 2.5 GeV electron beam at 80-100 mA. Intensity of the incident radiation was registered using ionization chamber filled with nitrogen. A silicon diode with avalanche amplification by FMB Oxford (UK) located at 90º to the beam was used as a fluorescence detector. Ionization chambers filled with argon were used as transmission detectors. The beam size on the sample was 1 mm^2. A silicon monoblock crystal with a slot forming two reflecting (220) surfaces was used as a monochromator.

Calibration of the X-ray absorption spectra of ThO_2 film and thorium-containing murataite ceramics was done taking into account the Th $4f_{7/2}$ and Th $2p_{3/2}$ binding energies of metallic thorium being 335.2 eV and 16300.3 eV [S2], respectively and the Th $4f_{7/2}$ binding energies in the film and ceramics being 334.4 eV and 334.0 eV, respectively measured earlier by XPS [S3, S4]. With these data in mind, the absorption edges E_0 16299.5 eV and 16299.1 eV in the spectra of ThO_2 and ceramics, respectively were chosen.

Since the composition and the structure of the first coordination sphere of thorium in ceramics and ThO_2 film were suggested to be the same, the spectra were processed using the Athena program [S5] in the same sequence: background subtraction; calibration by the Th L_{III}-edge shift; atomic absorption separation μ_0; Fourier transform with the weight coefficient k^3 in the range $k=2\div10$ $Å^{-1}$. The threshold energy was chosen by the first derivative of the L_{III} absorption edge, afterward, the ionization E_0 threshold energy was varied.

The normalized function $\chi(k)$ was calculated by (1):

$$\chi(k) = \frac{\mu(k)-\mu_0(k)}{\mu_0(k)}, \quad (1)$$

where $\mu(k)$ is the experimentally measured absorption coefficient, $\mu_0(k)$ – absorption coefficient of a free atom modelled by a set of cubic splines, k – photoelectron wave number.

The number of independent parameters (N_{ind}) was calculated by (2):

$$N_{ind} = 2\Delta k \Delta r/\pi, \quad (2)$$

where Δk and Δr reflect the number of independent points in the k and R spaces, respectively. The value of the amplitude reduction factor $S_0^2 = 0{,}9$ was fixed.

The modeling was done by the functional minimization (3):

$$\chi^2_\nu = \frac{N_{ind}}{\nu N_{pts}} \sum_{i=1}^{N_{pts}} \frac{(\chi_{data}(R_i)-\chi_{th}(R_i))^2}{\varepsilon_i^2} \quad (3),$$

where N_{pts} is the number of points in the fitted range, ν is the number of degrees of freedom, $\chi_{data}(r_i)$ and $\chi_{th}(r_i)$ are the calculated and experimental EXAFS-response respectively, ε_i is the measurement uncertainty associated with point *i*.

The modeling quality was determined by the R-factor (R_f) (absolute standard deviation between the model and experimental spectra). The R-factor (R_f) was calculated by (4):

$$R_f = \sum_{i=1}^{N_{pts}} \frac{[Re(\chi_{data}(R_i)-\chi_{th}(R_i))]^2+[Im(\chi_{data}(R_i)-\chi_{th}(R_i))]^2}{[Re(\chi_{data}(R_i))]^2+[Im(\chi_{data}(R_i))]^2}, \quad (4)$$

where N_{pts} is the number of points in the modeling range, $\chi_{th}(R_i)$ and $\chi_{data}(R_i)$ are the calculated and experimental EXAFS signal, respectively. It has to be noted that R_f is the lower, the higher modeling reliability is.

Spectra modeling was done in the R-space using Artemis program [S5].

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