ROBL-CRG	**Experiment title:** EXAFS / XANES investigations of K volume-doped $CoTiO_3$	**Experiment number**: 20-01-697
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Scientific Background

The climate relevant exhaust gases of automobiles powered by fossil fuels are of topical public interest. One way to reduce these emissions is the usage of fuels based on regenerative sources. Such fuels will contain an increasing amount of ethanol, e.g. up to 10 % in Germany and 85 % in USA. For the purpose of engine management and exhaust after-treatment, specific in-situ gas sensors are required, which operate under these harsh conditions at elevated temperature. Fot that reason chemiresistors [1] appear to be tailor-made as in-situ ethanol-sensors. By the application of high-throughput impedance spectroscopy (HTIS) [2] K-doped $CoTiO_3$ was identified as the most promising material due to response behaviour and reproducibility [3]. Polycrystalline $CoTiO_3$ samples with different K amounts were prepared via a polyol-mediated synthesis and calcinated. Further detailed investigations of the influence of K-doping on the atomic structure will ultimatively enhance the comprehension of the complex interactions between the active sensing surface and the ambient gas atmosphere.

Experiments

The coordination chemistry and lattice structure of 2 at% K-doped $CoTiO_3$ is of particular interest with respect to the specific position of the potassium ions in the volume-doped material. Therefore, Ti-K edge and Co-K edge XANES and EXAFS spectroscopy was employed to investigate the electronic and molecular structure of Ti and Co in pristine and K-doped CoTiO3 samples ($K \leq 15$ at%). The samples were measured as BN pellets in transmission mode at 15 K using a closed-cycle He cryostat. Data reduction and shell fitting was performed with WinXAS, using theoretical phase-shift and amplitude function calculated by FEFF8.2. The XANES and EXAFS spectra were also analyzed chemometrically using the ITFA software [4].

Results

Both Co-XANES and Ti-XANES showed no change with K-doping (Fig. 1), hence there is no detectable influence of K-doping on the electronic structure of these two elements. The same is true for the series of Co-EXAFS spectra, suggesting no change of the local structure around Co within the detection limit of the method. In contrast, the ITFA analysis showed four statistically significant components in the Ti-EXAFS spectra. The 2 at% K containing sample 3 is clearly discriminated from all other samples by factor 4 (Fig. 2, right). This factor is characterized by FT peaks in the 1 to 2.5 Å range (distance uncorrected for phase shift). The shell fit results in Table 1 showing significant structural changes of sample 3 versus the undoped sample 1, a shortening of the Ti-Co distance at 2.90 Å, and an extension of the Ti-Co distance at 3.44 Å.

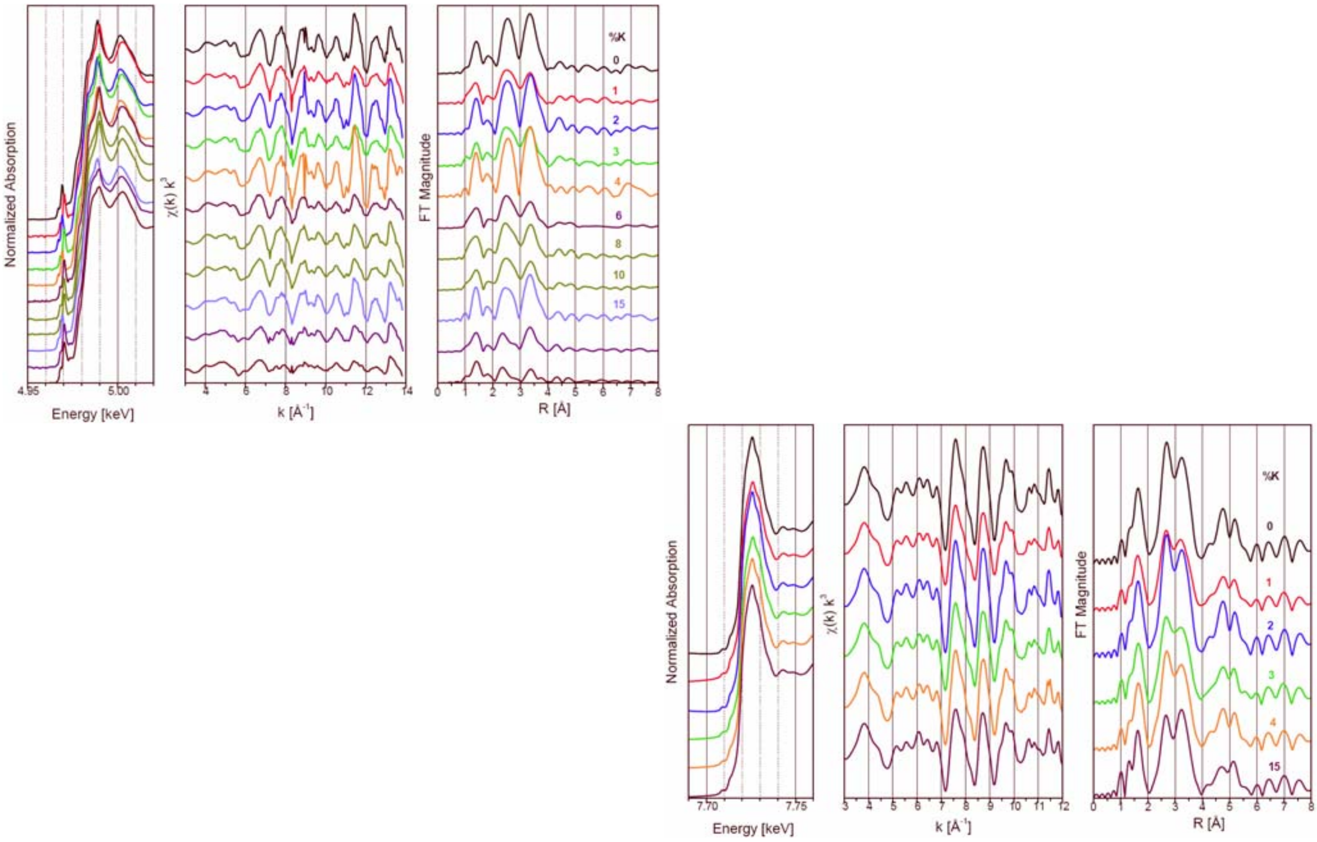

Fig. 1: Ti (left) and Co (right) K-edge XANES and EXAFS spectra as well as Fourier transform of volume-doped CoTiO$_3$ samples with different amounts of K dopant (0-15 %) at room temperature and ambient conditions.

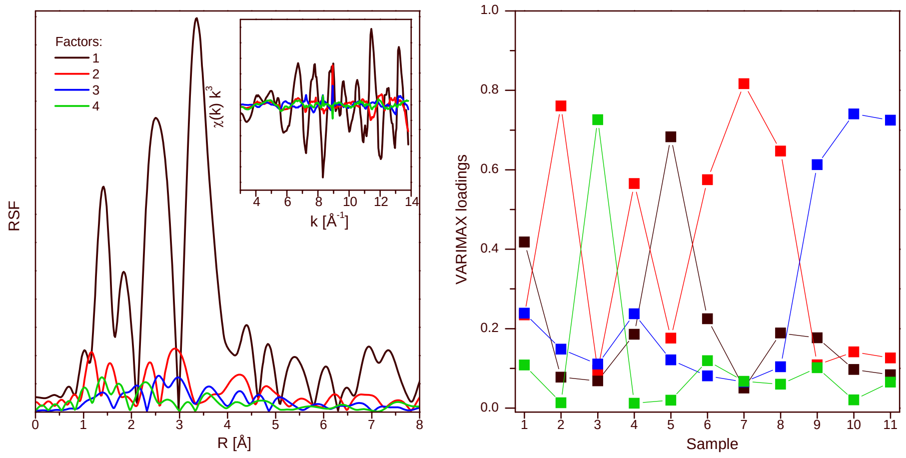

Fig. 2. Ti-K EXAFS factor analysis. Left: Factors 1 to 4 in R-space and in k-space (insert). Right: Varimax loadings of factors 1 to 4.

Table 1. Ti-K EXAFS shell fit results in comparison to the CoTiO$_3$ structure.

	CoTiO$_3$ XRD	AK-1 EXAFS	AK-1 EXAFS	AK-3 EXAFS	AK-3 EXAFS

	R / Å	R / Å	σ^2 / Å^2	R / Å	σ^2 / Å^2
3 O	1.87	1.87	0.0010	1.86	0.0010
3 O	2.09	2.08	0.0029	2.06	0.0031
1 Co	2.92	2.90	0.0010	2.87	0.0010
3 Ti	2.98	3.01	0.0017	3.00	0.0012
3 Co	3.39	3.44	0.0077	3.51	0.0071
6 Co	3.74	3.74	0.0018	3.73	0.0010

Literature

[1] M. E. Franke, T. J. Koplin, U. Simon, *Small* **2006**, *2(1)*, 110-118.
[2] M. Siemons, T. J. Koplin, U. Simon, *Appl. Surf. Sci.* **2007**, 254(3), 669-676.
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[4] A. Rossberg; T. Reich, G. Bernhard, *Anal. Bioanal. Chem.* **2003**, *376*, 631-638.