

EXAFS investigations of the local coordination geometry in oxynitrides $AB(O,N)_3$

S. G. Ebbinghaus¹, R. Aguiar², S. Riegg², A. Weidenkaff³

¹ Institut für Chemie, Martin-Luther Universität Halle-Wittenberg, Kurt-Mothes-Str. 2, 06120 Halle/Saale, Germany

² Lehrstuhl für Festkörperchemie, Universität Augsburg, Universitätsstraße 1, 86159 Augsburg, Germany

³ Solid State Chemistry and Catalysis, Empa, Ueberlandstrasse 129, 8600 Dübendorf, Switzerland

Perovskite-related oxynitrides of the general composition $ABO_{3-x}N_x$ are known since the mid-eighties [1]. Recently, unusual high dielectric permittivities ($\epsilon > 10^3$) were observed for a number of oxynitrides [2]. These high ϵ -values were found to be almost independent of temperature and frequency. Since diffraction experiments show that the respective compounds crystallize in centrosymmetric space groups (e.g. Figure 1) it has been argued that the large dielectric constants result from local dipoles due to different metal–nitrogen and metal–oxygen bond lengths [3].

To address this question we performed EXAFS measurements at the K- and L_{III} -edges of the transition metals of different samples including $SrTaO_2N$, $SrNbO_2N$, $LaTiO_2N$, $NdTiO_2N$, and $LaTaON_2$. Depending on the edge energies these measurements were carried out at beamlines E4, C1, A1 and X1 in transmission mode.

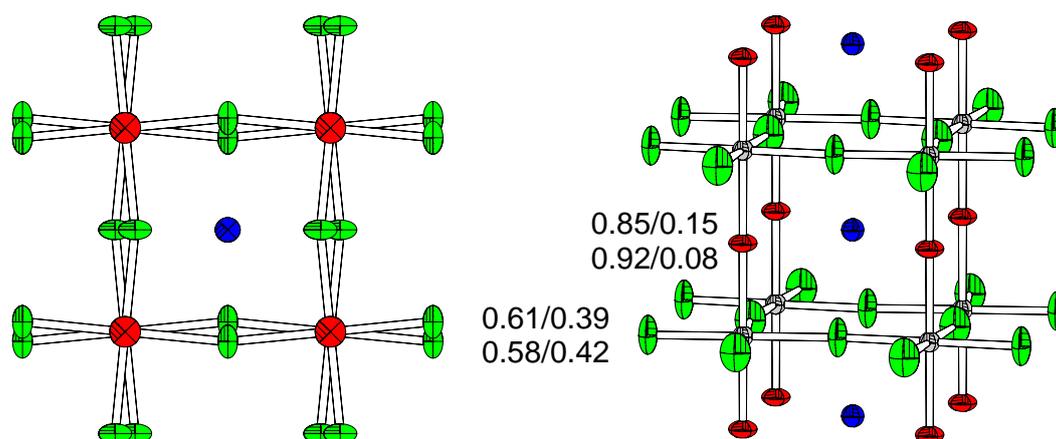


Figure 1: Section of the crystal structure of $SrNbO_2N$ (space group $I4/mcm$) as derived from powder neutron diffraction viewed along the c -axis (left) and almost along the a -axis (right). Displacement parameters are shown at the 90 % probability level. Numbers indicate the fractional O/N site occupation factors for a slowly cooled and a quenched sample (upper and lower values, respectively).

As an example, Figure 2 depicts the absorption spectrum of $SrTaO_2N$ at the Ta- L_{III} edge, the extracted EXAFS function $\chi(k)k^2$ and its Fourier transform. The first coordination sphere, which corresponds to the Ta-(O,N)₆ unit, was fitted using different models. In all trials the total coordination number was fixed to six. The simplest description by 6 identical atoms resulted in an unusual large Debye-Waller factor and a poor fit. Including an anharmonicity (3rd cumulant) did not significantly increase the quality of the fit. This indicates that the applied model was insufficient. For this reason, a two-shell model was used. Since in $SrTaO_2N$ every Ta ion is surrounded by 4 oxygen and 2 nitrogen ions, two different distances were considered and the coordination numbers were fixed to 4 and 2, respectively. To reduce the number of free parameters, equal Debye-Waller factors and E_0 values were used for both shells. The resulting distances of the

two backscattering shells differ significantly by about 0.1 Å, in good agreement with theoretical calculations [4] and EXAFS results from a different group [3]. The average bond length agrees very well with values derived from diffraction techniques. It is noteworthy that due to the almost identical backscattering amplitudes and phase shifts of oxygen and nitrogen the results remain basically the same if N and O are exchanged: We found two shorter and four longer bonds (with a difference of roughly 0.1 Å) for all possible atomic combinations (2·N+4·O; 2·N+4·N, 2·O+4·O, and 2·O+4·N). The assignment of the shorter distance to the Ta–N bond was done on the basis of plausibility and should not be considered a proof. Nevertheless, from our results it follows that different bond lengths can indeed be the origin of the high permittivities found for oxynitride perovskites.

Since neutron diffraction indicate almost equal Ta–(O,N) distances [5-7], it can furthermore be concluded that only on the local scale the Ta–N distance is significant shorter than the Ta–O distance, while on the larger scale relevant for diffraction experiments the differences average out.

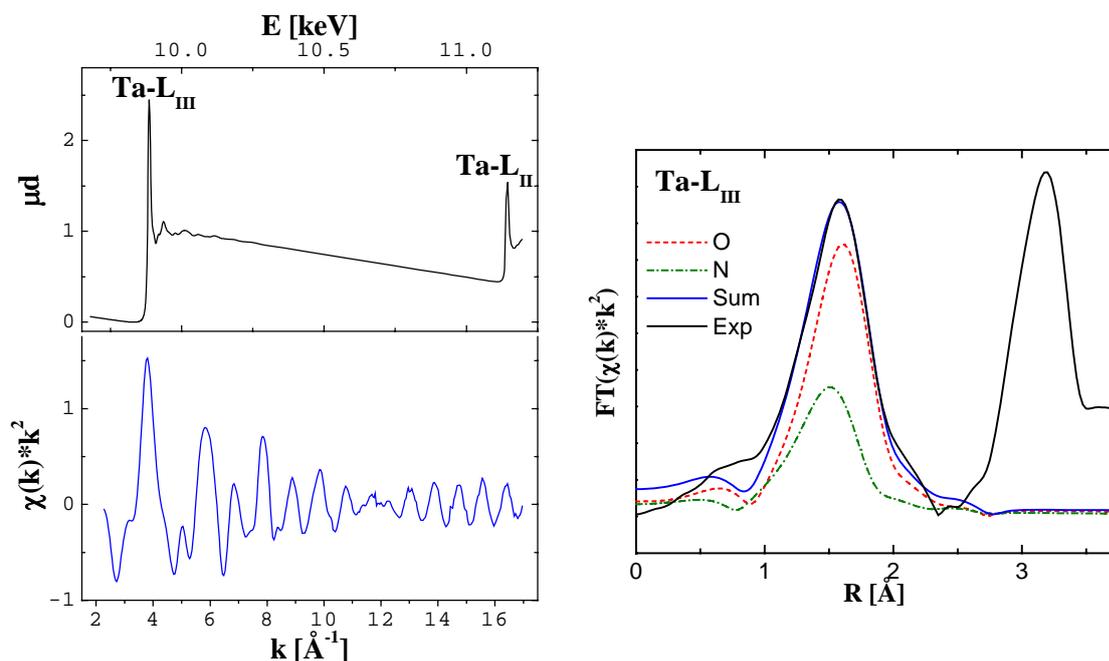


Figure 2 left: Normalized X-ray absorption spectrum of SrTaO₂N (top) and extracted k^2 -weighted EXAFS function (bottom). Right: Fourier transform and fit of the first coordination shell.

References

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