In contrast to cation substitutions, which have been studied extensively since decades, rather little is known about anionic substitutions in perovskites. Especially nitrogen-substituted perovskites are, on the other hand, highly interesting because their unusual optical properties and chemical stability make them promising candidates as pigments [1] or as photocatalysts, e.g. in the light-induced water splitting reaction [2]. In analogy to oxide perovskites, many structural modifications of the archetype cubic perovskite structure are known for oxynitrides. Since oxygen and nitrogen ions differ in size and charge, a possible ordering of these anions has to be considered. SrNbO$_2$N for example possesses a tetragonal unit cell (figure 1) with a partial ordering of oxygen and nitrogen [3].

While the perovskite-related oxides of titanium, niobium and tantalum (e.g. SrNbO$_3.5$ or LaTiO$_3.5$) are colourless, the corresponding oxynitrides (SrNbO$_2$N, LaTiO$_2$N) show very intense colours. It has been argued that this change of colour results from the more covalent character of the $M$–$N$ bond with respect to the $M$–$O$ bond. This higher covalence reduces the electronic band gap and shifts the electronic transitions to the visible region of the electromagnetic spectrum.

To investigate the electronic structure of our oxynitride perovskites we performed XANES measurements at the L$_{2,3}$-thresholds of the transition metals. The X-ray spectra at these absorption edges are dominated by very intense white lines, which are due to dipole-allowed transitions from the P$_{1/2,3/2}$ ground states to unoccupied states with predominantly d-character. As a result, these white lines yield detailed information on the electronic configuration of the corresponding metals. For instance, an increase of the oxidation state of the transition metals leads to a shift of the white lines to higher energy [4]. This effect known as the valence shift.

![Figure 1: Crystal structure of SrNbO$_2$N derived from neutron diffraction.](image1.png)

![Figure 2: Ta-L$_3$ XANES of CaTaO$_2$N, Ca$_2$Ta$_2$O$_7$ and CaTa$_2$O$_6$.](image2.png)
Figure 2 shows a comparison of the Ta–L₃ XANES of CaTaO₂N with the related oxides Ca₂Ta₂O₇ and CaTa₂O₆. As can be seen, the energy of the white line is identical for the two oxides while it is shifted towards lower energies for the oxynitride. Similar results were obtained for other pairs of samples like Sr₂Ta₂O₇/SrTaO₂N or LaTaO₄/LaTaON₂. Obviously, this shift is caused by the partial substitution of oxygen by nitrogen. It is worth noting that in the examined samples this substitution does not influence the oxidation state of the transition metal. Therefore, the shift is purely due to the so-called chemical shift and directly reflects the higher covalent character of the metal–nitrogen bond.

![Figure 2: Ta–L₃ XANES of CaTaO₂N with related oxides Ca₂Ta₂O₇ and CaTa₂O₆.](image)

In addition to classical solid state synthesis we also prepare nanocrystalline oxynitrides using different soft-chemistry approaches. The obtained compounds usually show very broad X-ray and neutron diffraction peaks making it difficult to gain structural information by Rietveld analysis. We therefore use EXAFS spectroscopy as a complementary method to investigate the crystal structure of our nanocrystalline oxynitrides. In the left side of figure 3 the Ta-L absorption spectrum of SrTaO₂N is depicted together with the extracted \( \chi(k)k^3 \). The right part of the figure shows the corresponding Fourier transform together with the results of the fit. A very good agreement between the EXAFS results and interatomic distances given in the literature was found for the O/N and Sr shell. Only for the Ta shell a larger deviation was observed. Given the small magnitude of the corresponding peaks in the Fourier transform this result is not surprising.

![Figure 3: Ta-L₃ EXAFS results for SrTaO₂N.](image)

References