Band Gap Engineering in Photocatalysts by Anion Substitution: from $Ba_3Ta_5O_{15}$ to $Ba_3Ta_5O_{14}N$

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Barium tantalum compounds are well-known photocatalysts for water splitting.[1] Interestingly, also the gray mixed-valance compound $Ba_3Ta^{V}_4Ta^{IV}O_{15}$ showed significant photocatalytic activity.[2] One approach to optimize the activity is band-gap narrowing by exchange of oxide with nitride ions and simultaneous oxidation of the tantalum(IV) ions.
We successfully synthesized light yellow $Ba_3Ta_5O_{14}N$ (tantalum(V) only!) as pure-phase material crystallizing isostructurally to the known mixed-valence oxide $Ba_3Ta_5O_{15}$ (see Fig. 1).
The electronic structure of $Ba_3Ta_5O_{14}N$ was studied theoretically with a hybrid Hartree–Fock-DFT method. Successively, two nitride ions were placed on two of the Wyckoff positions 2*d*, 4*h*, 8*i*, and 8*j*. The most stable structure was obtained when they were placed at 4*h* sites having fourfold coordination.
By incorporating nitride, the band gap decreases to 2.9 eV, giving rise to an absorption band well in the visible-light region (see Fig. 2). $Ba_3Ta_5O_{14}N$ was also tested for photocatalytic hydrogen generation.

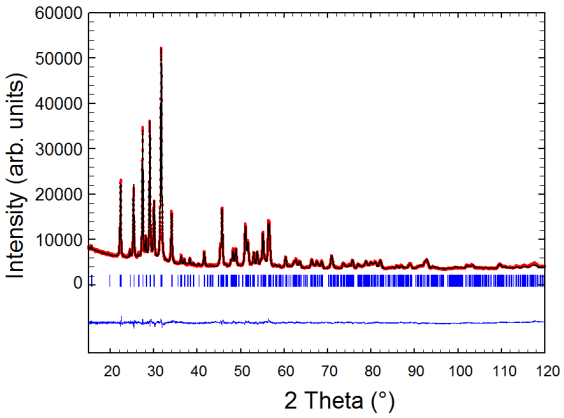

Figure 1: X-ray powder diffraction pattern of $Ba_3Ta_5O_{14}N$ with the results of the Rietveld refinement.

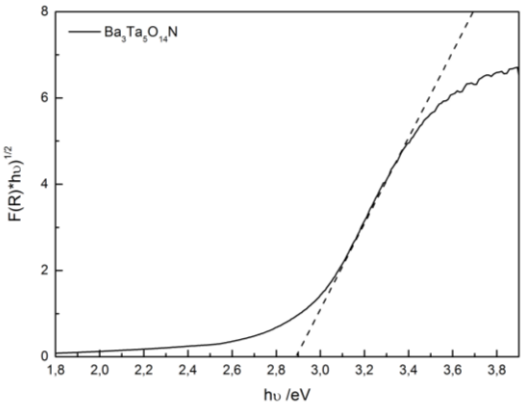

Figure 2: UV/Vis spectrum $Ba_3Ta_5O_{14}N$ as derived from a diffuse reflectance measurement.

References

[1] a) R. Marschall, J. Soldat, M. Wark, *Photochem. Photobiol. Sci.* **2013**, *12*, 671–677; b) J. Soldat, M. Wark, R. Marschall, *Chem. Sci.* **2014**, DOI: 10.1039/c4sc01127a.
[2] C. Feger, R. Ziebarth, *Chem. Mater.* **1995**, *7*, 373–378.