

# Band Gap Engineering in Photocatalysts by Anion Substitution: from $\text{Ba}_3\text{Ta}_5\text{O}_{15}$ to $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$

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Barium tantalum compounds are well-known photocatalysts for water splitting.[1] Interestingly, also the gray mixed-valence compound  $\text{Ba}_3\text{Ta}^{\text{V}}_4\text{Ta}^{\text{IV}}\text{O}_{15}$  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  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  (tantalum(V) only!) as pure-phase material crystallizing isostructurally to the known mixed-valence oxide  $\text{Ba}_3\text{Ta}_5\text{O}_{15}$  (see Fig. 1).

The electronic structure of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  was studied theoretically with a hybrid Hartree–Fock–DFT method. Successively, two nitride ions were placed on two of the Wyckoff positions  $2d$ ,  $4h$ ,  $8i$ , and  $8j$ . The most stable structure was obtained when they were placed at  $4h$  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).  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  was also tested for photocatalytic hydrogen generation.

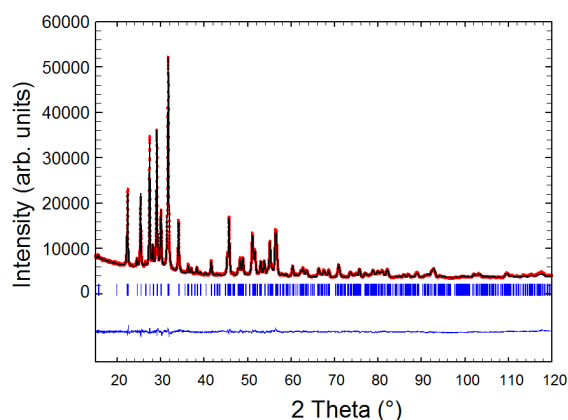


Figure 1: X-ray powder diffraction pattern of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  with the results of the Rietveld refinement.

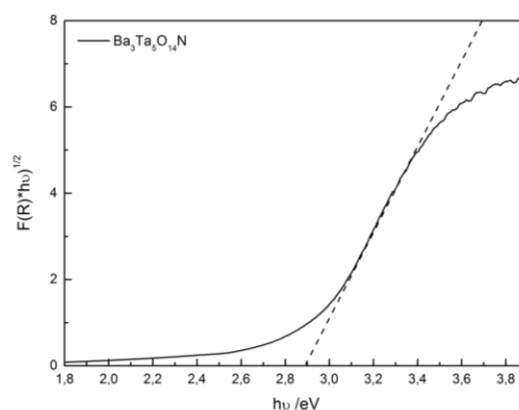


Figure 2: UV/Vis spectrum  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  as derived from a diffuse reflectance measurement.

## 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.