Band Gap Engineering in Photocatalysts by Anion Substitution: from Ba₃Ta₅O₁₅ to Ba₃Ta₅O₁₄N

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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 Ba₃Ta₅O₁₄N 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). Ba₃Ta₅O₁₄N was also tested for photocatalytic hydrogen generation.

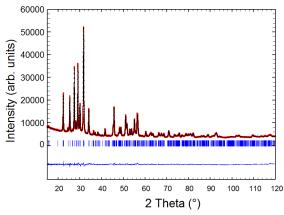


Figure 1: X-ray powder diffraction pattern of $Ba_3Ta_5O_{14}N$ with the results of the Rietveld refinement.

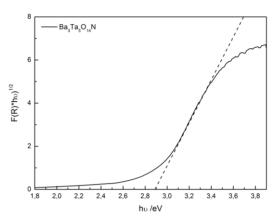


Figure 2: UV/Vis spectrum Ba₃Ta₅O₁₄N as derived from a diffuse reflectance measurement.

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References

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