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Band Gap Adjustment in Perovskite-type $\text{Eu}_{1-x}\text{Ca}_x\text{TiO}_3$ via Ammonolysis

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Abstract: Perovskite-type oxynitrides $AB(\text{O},\text{N})_3$ are potential candidates for photoelectrode materials in solar water splitting. A drawback of these materials is their low sintering tendency resulting in low electrical conductivities. Typically, they are prepared by ammonia treatment of insulating, wide band gap oxides. In this study, we propose an approach starting from small band gap oxides $\text{Eu}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$ and then widen the band gaps in a controlled way by ammonolysis and partial Ca^{2+} substitution. Both together induced a distortion of the octahedral network and dilution of the $\text{Eu}4f$ and $\text{N}2p$ levels in the valence band. The effect is the stronger the more Ca^{2+} is present. Within the series of samples, $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ had the most suitable optical band gap ($E_G \approx 2.2$ eV) for water oxidation. However, its higher Eu content compared to $\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$ slowed down the charge carrier dynamics due to enhanced trapping and recombination as expressed by large accumulation (τ_{on}) and decay (τ_{off}) times of the photovoltage of up to 109 s and 486 s, respectively. In contrast, the highly Ca^{2+} -substituted

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samples ($x \geq 0.7$) were more prone to formation of TiN and oxygen vacancies also leading to Ti^{3+} donor levels below the conduction band. Therefore, a precise control of the ammonolysis temperature is essential, since even small amounts of TiN can suppress the photovoltage generation by fast recombination processes. Water oxidation tests on $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ revealed a formation of $7.5 \mu\text{mol O}_2$ from 50 mg powder together with significant photocorrosion of the bare material. Combining crystal structure, chemical composition, and optical and electronic band gap data, a first simplified model of the electronic band structure of $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ could be proposed.

Keywords: Electronic band structure; europium; oxynitride; perovskite; surface photovoltage spectroscopy; titanium.

1 Introduction

Perovskite-type oxynitrides $\text{AB}(\text{O},\text{N})_3$ are potential candidates as light absorbers/ photocatalysts and photoanodes in the photoelectrolysis of water producing oxygen and hydrogen fuel. Typically, these oxynitrides contain Ca^{2+} , Sr^{2+} , Ba^{2+} or La^{3+} on the A-site and Ti^{4+} , Nb^{5+} or Ta^{5+} on the B-site of the perovskite-type structure [1–32]. Recently, we reported on several new perovskite-type family members with rather unusual cations on the A- and/or B-site position such as Mg^{2+} , Y^{3+} , Zr^{4+} or Ta^{4+} providing new opportunities to adjust the optical band gap [33, 34]. An alternative approach to ensure charge compensation during the N incorporation into perovskite-type oxides ABO_3 ($\text{A} = \text{Ca}^{2+}$, Sr^{2+} , Ba^{2+} ; $\text{B} = \text{Ti}^{4+}$, Zr^{4+}) was tested. Therefore, a double anionic substitution of F^- and N^{3-} for O^{2-} was used [35, 36]. For all these materials the synthesis started from insulating, typically white, wide band gap oxides, the band gap was reduced by N incorporation to roughly 2 eV as required for improved solar energy conversion [24, 37]. In many reported cases sophisticated electrode engineering using an adjusted sequence of substrate, light-absorber, necking material, protection layers, and cocatalysts was required to significantly improve the photocurrent of the photoanodes [18, 38–44]. However, the overall performance is still limited due to the poor compaction and sintering of most oxynitrides. Often a so-called necking procedure, e.g. with TiN, is used to ensure proper electrical contact between the oxynitride grains/particles [39, 41, 45]. These conductive pathways carry the risk to act as recombination centers for the photoinduced charge carriers.

An approach to overcome these limitations is to start with a well-sinterable (semi)-conducting oxide and widen the band gap in a controlled way up to approximately 2 eV. The thermoelectric perovskite-type oxide $\text{Eu}(+\text{II})\text{Ti}(+\text{IV})\text{O}_{3-\delta}$ has

been identified as an interesting compound for this approach. In contrast to the structurally closely related SrTiO_3 , EuTiO_3 has a small band gap of only $E_G = 0.98$ eV [46–50] due to the presence of sharp Eu 4*f* electronic states close to the Fermi level. Unlike the usually observed band gap reduction upon partial substitution of N for O, ammonolysis of EuTiO_3 resulted in an unexpected band gap widening. This can be explained by the partial formation of Eu^{3+} in consequence of compensating for the additional negative charge (N^{3-} vs. O^{2-}). The formation of Eu^{3+} was confirmed by X-ray photoelectron spectroscopy (XPS) on $\text{EuTi}(\text{O},\text{N})_3$ [48] and ^{151}Eu Mössbauer spectroscopy on EuTiO_2N [51]. The presence of the smaller Eu^{3+} ($r(\text{Eu}^{3+}) = 129.5$ pm, coordination number (CN) = 12) [52] in comparison to Eu^{2+} ($r(\text{Eu}^{2+}) = 144$ pm, CN = 12) [52] leads to distortion of the perovskite-type octahedral network in order to maintain the contact between the anions and A-site cations [50]. As with SrTiO_3 and CaTiO_3 , this results in a symmetry reduction from cubic to orthorhombic [53, 54]. As a consequence, the electronic band structure is modified and the Eu 4*f* states move away from the Fermi level widening the band gap to values of $E_G = 1.4$ – 1.5 eV [48]. As demonstrated by our previous studies, partial substitution of A^{2+} ($\text{A} = \text{Ba}^{2+}, \text{Ca}^{2+}$) for Eu^{2+} is an effective strategy to further adjust the crystal structure and with it the electronic band structure, the band gap, as well as the charge carrier transport properties [50, 55]. It is well-known that (partial) substitution of a smaller cation on the A-site reduces the overlap of the O/N 2*p*-orbitals and the typically empty *nd*-orbitals ($n = 3, 4, 5$; principal quantum number) of the B-site cations leading to a smaller dispersion of the conduction band and hence a widening of the band gap [33, 56]. The formation of $\text{Eu}_{1-x}\text{Ca}_x\text{Ta}(\text{O},\text{N})_3$ [4] and $\text{Eu}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$ [50] solid solutions was demonstrated for the entire Ca^{2+} concentration range ($0 \leq x \leq 1$). The increased chemical pressure with increasing Ca^{2+} substitution was revealed in $\text{Eu}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$ forcing a stronger distortion of the octahedral network. As the coordination sphere was now more suitable for Eu^{3+} compared to the larger Eu^{2+} , this had a self-enhancing effect on the Eu^{3+} content clearly modifying the localization of the Eu 4*f* levels and the band gaps [50]. Besides the electronic band structure (band edges and gap), also the dynamics of the photogenerated charge carriers are of fundamental interest for photoanode applications. The charge carrier dynamics and recombination behavior are often investigated by surface photovoltage spectroscopy (SPS) providing information about the majority charge carriers, effective band gaps, charge carrier transfer rates and charge carrier trapping [30, 57–61].

Here, we present a synthesis method for perovskite-type oxynitrides as potential photoanodes for water oxidation. The yellow to green oxynitrides $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ were synthesized via thermal gas flow ammonolysis of the well-sinterable, small band gap, perovskite-type oxides $\text{Eu}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$ ($0 < x < 1$). Their band gap size of 1.6 eV–2.6 eV is suitable for photoinduced water oxidation

applications. The effect of TiN and Eu 4f levels on the charge carrier separation was studied. Combining the data of X-ray diffraction (XRD), chemical analysis, diffuse reflectance spectroscopy (DRS), surface photovoltage spectroscopy (SPS), and electrical resistivity and Seebeck coefficient measurements, a first simplified model of the electronic band structure of the perovskite-type oxynitrides $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ could be proposed.

2 Experimental

2.1 Sample preparation

Solid solutions with the general formula $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$) were synthesized by a soft chemistry route and subsequent annealing in different atmospheres. The samples were produced by taking stoichiometric amounts of europium(III) oxide (Alfa Aesar, $\geq 99.99\%$), titanium(IV)bis(ammonium dilactato)dihydroxide (Sigma Aldrich, 50 wt.% solution in water) and calcium nitrate tetrahydrate (Merck, $\geq 99.9\%$). Citric acid (Sigma Aldrich, $\geq 99.5\%$) and ethylene glycol (Merck, $\geq 99.5\%$) were used as complexing and gelling agent, respectively. Detailed information about the synthesis procedure of the nanocrystalline oxide precursors (NCP) have been described previously [50]. $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ with $x = 0.1, 0.3, 0.5, 0.7, 0.9$ were prepared by directly ammonolyzing the nanocrystalline oxide precursors, while for the samples with $x = 0.2, 0.4, 0.6, 0.8$ ammonolysis was carried out after crystallizing the perovskite oxide resulting in a microcrystalline precursor (MCP). In the latter case, powders were treated in forming gas (Westfalen, 95 vol.% N_2 , 5 vol.% H_2) at 1273 K for 12 h. Ammonolysis of both sets of samples was carried out in flowing ammonia (Westfalen, $\geq 99.98\%$) at 1073 K for 10 h using a gas flow rate of $100 \text{ mL} \cdot \text{min}^{-1}$. For selected samples the ammonolysis temperature was varied between 873 K and 1273 K. To study the influence of TiN on the charge carrier separation and recombination behavior of selected samples, 20 mol.% of titanium(IV)bis(ammonium dilactato)dihydroxide was added to induce the *in situ* formation of TiN.

In addition to powder samples, pellets with varying A-site compositions ($x = 0.2, 0.4, 0.6, 0.8$) containing TiN as sintering aid ($w(\text{TiN}) \leq 3.6(3) \text{ wt.}\%$) were produced. For that, the nanocrystalline precursors were pelletized using a uniaxial press (P/O/Weber PW20) prior to crystallization. Subsequently, the pellets were isostatically cold-pressed (P/O/Weber) with a pressure of 1.2 MPa and sintered under the same conditions as for crystallization. The resulting oxide pellets were ammonolyzed at 1173 K for 16 h. In order to measure the electrical transport

properties, the pellet was cut in bars of $14 \times 3 \times 3 \text{ mm}^3$ using a diamond wire cutting tool.

2.2 Materials characterization

The structural characterization of the produced oxide and oxynitride materials was carried out using a Rigaku Smartlab Bragg-Brentano diffractometer with Ni-filtered $\text{Cu-K}\alpha_{1,2}$ radiation. Rietveld refinements were carried out using the *Full-Prof* 2.k program suite [62] and pseudo-Voigt functions to describe the reflection profile. All powder X-ray diffraction patterns were refined as oxides reducing the number of parameters due to the virtually equal atomic form factors of N^{3-} and O^{2-} .

The anionic composition was determined by carbothermal fusion using the hot gas extraction technique (Eltra ONH-2000 and LECO ONH836 analyzer). Each sample was measured at least three times. Experimental densities of the compacted disks were determined by He gas pycnometry (AccuPyc II 1340, Micromeritics) and Archimedes principle measurements in deionized water. Microstructural analysis was carried by scanning electron microscopy (Zeiss GeminiSEM 500) with the InLens detector at 1.5 kV and 10 kV acceleration voltage, respectively. The electrical resistivity (ρ) and the Seebeck coefficients (S) were measured simultaneously using a Seebeck coefficient/electric resistance measurement system (ZEM-3, Ulvac Riko) from ambient temperature to 973 K in a nitrogen gas atmosphere.

UV-visible diffuse reflectance spectra (DRS) were obtained using a Carry 5000 UV-VIS NIR or an AJ&M TIDAS spectrophotometer. The baseline was measured with BaSO_4 . The spectra were recorded in the range of 200 nm–800 nm. The Kubelka-Munk conversion [63] was applied to the obtained reflectance spectra. The optical band gaps were determined by extrapolating the onset of absorption to the abscissa [47].

Fluorine-doped tin oxide (FTO) substrates ($12\text{--}14 \text{ } \Omega/\text{sq.}$, MTI Corporation) were cleaned by sonication in acetone, methanol, isopropanol, and water (purified to about $18 \text{ M}\Omega \cdot \text{cm}$ resistivity with a Nano-pure filtration system) for 10 min each, and subsequently dried in air. Suspensions of the $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ powders in water with a concentration of $0.5 \text{ mg} \cdot \text{mL}^{-1}$ were prepared. After sonication for 15 min, 0.05 mL of each suspension was drop-coated onto the FTO substrates. The covered area ($0.5 \text{ cm} \times 0.5 \text{ cm}$) was controlled with a polyester masking tape (Cole Parmer). After drying at room temperature, the films were heated on a hot plate at 373 K for 90 min in air. Photos of the films are included in the Supporting Information (s. Figure S1, Supporting Information). The films were

between 1.3 μm and 1.7 μm thick as determined with a stylus-type Veeco Dektak profilometer.

Surface photovoltage spectroscopy (SPS) was carried out using a vibrating gold mesh Kelvin probe (3 mm diameter, Delta PHI Besocke) mounted 1 mm above the film samples. Samples were positioned inside a custom-made vacuum chamber ($p \approx 10^{-4}$ mbar by a Pfeiffer HiCube 80 Eco turbo pump station). Monochromatic radiation was supplied by a 150 W Xe lamp using an Oriel Cornerstone 130 monochromator ($I_0 \approx 1 \text{ mW} \cdot \text{cm}^{-2}$). The measurements were not compensated for the variable light intensity of the Xe lamp. A signal drift in the spectra was corrected by subtracting a dark background from the raw data. Contact Potential Difference (CPD) values were obtained by subtracting the CPD value in the dark. Effective band gaps were obtained based on the major photovoltage signals of the spectra using the tangential method. Reversibility of charge carrier separation was examined with light on/off scans at 3.1 eV monochromatic illumination.

For photocatalytic water oxidation tests of $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ 50 mg powder was suspended in 50 mL demineralized water containing 0.02 M sacrificial reagent. Three different sacrificial agents and pH values were tested: (i) $\text{Fe}(\text{NO}_3)_3$ at pH = 1.85, (ii) AgNO_3 at pH = 5.85, and (iii) NaIO_4 at pH = 6.54. The flask was sonicated and then connected to an air-tight irradiation setup with a Varian 3800 gas chromatograph. The air in the flask was repeatedly evacuated down to 60 torr and purged five times with Ar before commencing the measurements. The system was continuously irradiated with a 300 W Xe lamp (with an intensity of 273–285 $\text{mW} \cdot \text{cm}^{-2}$) with a 400 nm long-pass filter for 6 h.

3 Results and discussion

The oxide precursor solid solutions $\text{Eu}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$ ($0 < x < 1$) were formed in the entire range of compositions [50]. In a first step, it was evaluated if this also applies to the respective perovskite-type oxynitrides $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$. Ammonolysis of $\text{EuTiO}_{3-\delta}$ was reported at 1223 K [48], which according to our experience is too high and will lead with our setup to the formation of TiN [33]. Therefore, a first series of samples was ammonolyzed at 1073 K. In order to study the effect of precursor crystallinity (s. Figure S2) on the resulting nitrogen content, the oxynitrides with $x = 0.1, 0.3, 0.5, 0.7, 0.9$ were prepared from the nanocrystalline precursor (NCP), while the microcrystalline precursor (MCP) was used for the samples with $x = 0.2, 0.4, 0.6, 0.8$. All oxide precursors (nano- or microcrystalline) were successfully converted to the orthorhombic oxynitrides $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ (s. Figure 1, Figure S3, and Table S1). The samples

Fig. 1: Rietveld refinements of the crystal structures of $\text{Eu}_{1-x}\text{Ca}_x\text{Ti(O,N)}_3$ ammonolyzed at 1073 K in the orthorhombic space group-type $Pnma$. (a) $x = 0.1$, (b) $x = 0.5$, and (c) $x = 0.7$. (d) Unit cell volume depending on the Ca^{2+} content. The red line is the linear fit according to Vegard's law. The asterisks indicate residual $\text{Cu-K}\beta$ radiation. Further refinement results can be found in Figure S3.

prepared from the nanocrystalline precursors had slightly higher nitrogen contents than these from the microcrystalline precursor (s. Figure S5 and Table S4). This is in agreement with the expected easier ammonolysis of the metastable nanocrystalline precursor in comparison to the thermodynamically stable microcrystalline precursor. XRD measurements showed small Eu_2O_3 impurities in $\text{Eu}_{0.9}\text{Ca}_{0.1}\text{Ti(O,N)}_3$ indicating inadequate mixing of the starting materials during the oxide precursor synthesis. An increasing formation of TiN was observed in oxynitrides with Ca^{2+} contents higher than $x = 0.6$ (s. Figure 1 and Figure S3) evidenced by surprisingly high nitrogen contents (s. Figure S5 and Table S4).

This can be explained by a decrease of the Goldschmidt tolerance factor t with increasing Ca^{2+} substitution due to the smaller ionic radius of Ca^{2+} in comparison to Eu^{2+} [50]. Strongly associated with this is a reduction in the difference between the average bonding energy [ABE s. equation (1)] of the perovskite-type oxides

Fig. 2: Calculated average bonding energy (ABE , black squares) of $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ depending on the Ca^{2+} content together with the standard formation enthalpy of TiN [64]. For simplicity, all samples were treated as oxides $\text{Eu}_{1-x}\text{Ca}_x\text{TiO}_3$.

(taken for simplicity) and the formation enthalpy of TiN (s. Figure 2) [64–66]. Consequently, a higher Ca^{2+} content facilitates the formation of TiN .

$$ABE = \frac{1}{12m} \left(\Delta H_{A_m\text{O}_n}^0 - m \cdot \Delta H_A^0 - \frac{n}{2} \cdot D_{\text{O}_2}^0 \right) + \frac{1}{6k} \left(\Delta H_{B_k\text{O}_l}^0 - k \cdot \Delta H_B^0 - \frac{l}{2} \cdot D_{\text{O}_2}^0 \right) \quad (1)$$

where ABE equals the average bonding energy, m , n , k , l the stoichiometric coefficients, $\Delta H_{A_m\text{O}_n}^0$ and $\Delta H_{B_k\text{O}_l}^0$ the standard formation enthalpy of the binary oxides $A_m\text{O}_n$ and $B_k\text{O}_l$, respectively, ΔH_A^0 and ΔH_B^0 the respective standard sublimation enthalpies of the metals A and B , and $D_{\text{O}_2}^0$ the molar dissociation energy of oxygen molecules.

As further adjustment, the ammonolysis temperature for $\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$ was systematically lowered to 873 K in 50 K-steps. Indeed, PXRD patterns did not reveal any formation of TiN below 1023 K. Lowering the ammonolysis temperature below 923 K clearly reduced the crystallinity of the samples as expressed by the broadening of the reflections (s. Figure 3 and Table S2). For control purposes, two oxynitrides $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ were produced at 1048 K and 998 K, respectively. Both samples were TiN -free according to the Rietveld refinements of the PXRD patterns (s. Figure 4 and Table S3) indicating that a difference of more than 7.5% between the standard formation enthalpy of TiN and the average bonding

Fig. 3: Rietveld refinements of the crystal structures of $\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$ ammonolyzed at different temperatures in the orthorhombic space group-type $Pnma$. (a) $T = 873\text{ K}$, (b) $T = 923\text{ K}$, (c) $T = 973\text{ K}$, (d) $T = 1023\text{ K}$, and (e) $T = 1073\text{ K}$. The asterisks indicate residual $\text{Cu-K}\beta$ radiation.

energy of the perovskite phase is sufficient to suppress the formation of TiN in this temperature range.

The ammonolysis of $\text{Eu}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$ to form $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ requires a charge compensation since N^{3-} has higher negative charge in comparison to O^{2-} .

Fig. 4: Rietveld refinements of the crystal structures of $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ ammonolyzed at different temperatures in the orthorhombic space group-type $Pnma$. (a) $T = 998 \text{ K}$ and (b) $T = 1048 \text{ K}$. The asterisks indicate residual $\text{Cu-K}\beta$ radiation.

There are three fundamental ways during ammonolysis to do so: (i) aliovalent substitution on the A- or B-site with a cation of higher charge, (ii) oxidation of a cation if possible, e.g. Eu^{2+} to Eu^{3+} , (iii) formation of oxygen vacancies. The first option does not apply to $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$, since on the precursor level either an isovalent substitution (Ca^{2+} vs. Eu^{2+}) in the case of MCP or for NCP an aliovalent substitution with a cation of lower charge (Ca^{2+} vs. Eu^{3+}) was used. As shown by chemical analysis case (iii) plays a minor role and is only active at high Ca^{2+} contents ($x > 0.7$) leaving behind just the oxidation of Eu^{3+} as charge balancing mechanism. As can be seen from Table S4 and Figure S5 for $x < 0.5$ the Eu content is larger than the nitrogen content ($N_{\max} = 0.55 \pm 0.02$) requiring the presence of Eu^{2+} besides Eu^{3+} . However, for all $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ samples the +III state is dominating ($\text{Eu}_{\max}^{2+} = 0.42 \pm 0.02$). For calcium contents $0.5 \leq x \leq 0.6$ the nitrogen content equals the nitrogen content within experimental uncertainty hence requiring the solely presence of Eu^{3+} for charge balancing. At higher calcium content ($x > 0.6$) the situation becomes more complex and the system opens additional sideways during ammonolysis, e.g. at higher temperatures the formation TiN is observed and at lower temperatures the formation of oxygen vacancies happens in addition to compensate the higher nitrogen amount in the sample with respect to the Eu content. However, in both cases predominantly Eu^{3+} has to be present for charge balancing.

The size of the band gap is an important parameter for the water oxidation ability since it affects the light absorption behavior and the general thermodynamic feasibility of the water oxidation process. The oxynitrides obtained by ammonolysis at 1073 K had a dark color scheme. At low Ca^{2+} contents ($x < 0.5$) the samples had a brownish-black tone similar to the color of the oxide precursors.

Samples with higher Ca^{2+} contents ($x > 0.5$) were dark green lightening with increasing Ca^{2+} content (s. Figure S7). To obtain stronger DRS signals, the samples were diluted with NaCl. However, light absorption remained high (s. Figure S6), in particular at energies smaller than the optical band gap, indicating the presence of significant amounts of optically active defects. A common explanation for such a behavior in titanates is the presence of Ti^{3+} species such as TiN [7, 11, 29, 67, 68]. Since the respective PXRD patterns did not show any TiN for $x < 0.7$ (s. Figure 1 and Figure S3), it might be present as a thin (amorphous) surface layer arising from the rather high ammonolysis temperature. Additionally, an influence of the entropically forced presence of oxygen vacancies on the formation of Ti^{3+} within $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ cannot be excluded. For oxynitrides with even higher Ca^{2+} contents ($x \geq 0.7$), the contribution of TiN decreased as shown by the clear widening of the optical band gap (s. Figure S6 and Table S7). This can be attributed to an increased distortion of the octahedral network with increasing Ca^{2+} content as expressed by the larger orthorhombicity and the reduction of the Ti–X(1)–Ti and Ti–X(2)–Ti angles ($X = \text{O}, \text{N}$), respectively (s. Figure 5 and Figure S4). The orthorhombicity O is a quantitative measure describing the deviation of the a - and c -axis from a cubic subcell as given by equation (2) [69].

$$O_{a,c} = \frac{(a - c)}{(a + b)} \cdot 100\% \quad (2)$$

Among the samples, $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ (ammonolyzed at 1073 K) had the most promising optical band gap size for photoinduced water oxidation. The $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ samples ammonolyzed at lower temperatures (998 K and

Fig. 5: Average Ti–X–Ti angles ($X = \text{O}, \text{N}$; black squares) and orthorhombicity O (blue triangles) of $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ depending on the Ca^{2+} content.

1048 K) had an intensive yellow to light green color. Accordingly, the DRS measurements (s. Figure 6) revealed a much lower optically active defect concentration and an optical band gap of $E_G \approx 2.2$ eV. As expected by the increased tilting of the octahedral network, $\text{Eu}_{0.2}\text{Ca}_{0.8}\text{Ti}(\text{O},\text{N})_3$ ammonolyzed at 1073 K and $\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$ ammonolyzed in the temperature range of 923 K and 1023 K showed larger optical band gaps. According to the electronic band structure proposed by Sagarna et al. [48] larger Ca^{2+} contents lead to the dilution of the Eu 4*f* levels in the valence band. Additionally, the nitrogen content (s. Table S5) of these samples was lower resulting also in a smaller contribution of the N 2*p* levels to the valence band. Both effects are expected to result in a downward shift of the valence band edge and hence to a widening of the band gap. The optical band gap data are summarized in Table 1. The decreasing optical band gap of $\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$ with increasing ammonolysis temperature together with an

Fig. 6: DRS measurements of (a) $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ ammonolyzed at 998 K (blue) and 1048 K (red) and (b) $\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$ ammonolyzed at 923 K (black), 973 K (blue), and 1023 K (red), respectively.

Tab. 1: Summary of optical band gaps of selected $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ samples derived from DRS.

Material	Ammonolysis temperature (K)	Optical band gap E_G (eV)
$\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$	1073	2.22 ± 0.05
$\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$	1048	2.22 ± 0.05
$\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$	998	2.25 ± 0.05
$\text{Eu}_{0.2}\text{Ca}_{0.8}\text{Ti}(\text{O},\text{N})_3$	1073	2.53 ± 0.05
$\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$	1023	2.35 ± 0.08
$\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$	973	2.46 ± 0.07
$\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$	923	2.56 ± 0.08

increasing absorption at energies below the band gap could indicate a beginning and steadily increasing formation of TiN impurities.

The separation of photoinduced charge carriers in the materials, was determined by surface photovoltage spectroscopy (SPS) of thin films ($1.5 \pm 0.5 \mu\text{m}$) on FTO substrates under vacuum (s. Figure 7 and Table 2). In SPS, the contact potential difference (CPD) of a sample film is measured under illumination with a semi-transparent Kelvin probe [70–73]. The photovoltage (ΔCPD) is due to the movement of charge carriers from the light absorbing particles to the conductive substrate, or from trapping of carriers in particle surface states [74, 75]. These spectra give insight into majority carrier type, trap states, and the effective band gap of the semiconductor, without the need for any faradaic processes [61, 74–76]. As can be seen from Figure 7, all four samples showed a negative photovoltage indicating electron injection into the FTO substrate as seen for *n*-type semiconductors. The effective band gaps were obtained from the photovoltage spectra by the tangential method. All four samples showed an effective band gap of $2.30 \pm 0.05 \text{ eV}$ in agreement with their optical band gaps (s. Table 1 and Table S7). The 0.5–0.7 eV redshift of the photoonset for $\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$ (973 K) is attributed to sub gap donor levels, likely involving coupled Ti^{3+} and oxygen vacancy defects. The photovoltage decreased with decreasing Ca content and increasing ammonolysis temperature since both led to a decrease of the optical band gap (s. Table 1) and hence reducing the maximum achievable photovoltage. In particular a higher ammonolysis temperature favor defect formation, which can serve as recombination centers for photogenerated electron/hole pairs. An alternative explanation might be the

Fig. 7: (a) SPS data of $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ samples with $x = 0.6$ and 0.9 on FTO substrates. The extrapolated tangents were used to find the effective band gap. ΔCPD values are relative to the CPD in the dark. (b) Transient surface photovoltages using chopped light at 3.10 eV (on: $\sim 1500 \text{ s}$ mark; off: $\sim 1700\text{--}2000 \text{ s}$).

formation of TiN (below XRD detection limit) with increasing ammonolysis temperature as implied by the slightly higher N contents of these samples determined by HGE. Already less than 1 wt.% TiN added to the material is found to quench the photovoltage entirely (see also below). An additional influencing factor might be the presence of the $\text{Eu}^{2+} (4f^7)/\text{Eu}^{3+} (4f^6)$ redox couple. However, since chemical analysis of the anionic composition of these four samples revealed nitrogen contents equal ($x = 0.6$) or even higher ($x = 0.9$) than the Eu content, a significant presence of Eu^{2+} in these samples can be neglected for reasons of charge balance. The overstoichiometric nitrogen content of $\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$ ammonolyzed at 973 K and 1023 K, respectively, require the presence of oxygen vacancies and hence Ti^{3+} donor levels in the crystal structure and electronic band structure, respectively. The presence of oxygen vacancies was confirmed by hot gas extraction measurements (s. Table S5). Therefore, the influence of potentially remaining traces of Eu^{2+} on the photovoltage can be considered of secondary importance compared to the effect of Ti^{3+} .

Secondly, the reversibility and timescale of carrier separation was evaluated by applying chopped light scans under 3.1 eV monochromatic illumination to the samples (s. Figure 7b). The on- and off-times, τ_{on} and τ_{off} , in Table 2 refer to the times needed for the photovoltage to reach 63.2% of the final value after switching the light on or off. For all four samples, τ_{off} was much longer than τ_{on} , i.e. the return of the majority carriers into the films is slower than the injection into the substrate (FTO). This SPS result is common for powdered films. It is likely associated with trapping of minority carriers (holes) in defect states that are difficult to access by the electrons [61, 74]. We also note that charge separation is about 5 times faster in $\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$ than in $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$, which points to a higher concentration of majority carrier traps in the latter. From the observed increase of the optical band gap and the discussed correlation between photovoltage and TiN an opposite behavior would have been expected. This suggests that charge carrier generation and recombination times are strongly affected by the concentration and position of the Eu 4f levels in the electronic band structure [48].

Tab. 2: Summary of SPS measurement results of selected $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ samples.

Material	Ammonolysis temperature (K)	Photo onset (eV)	Effective band gap (eV)	Photovoltage (V)	τ_{on} (s)	τ_{off} (s)
$\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$	998	2.17	2.26	−0.83	75.2	485.6
$\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$	1048	2.33	2.33	−0.14	108.9	205.6
$\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$	973	1.74	2.26	−1.23	20.0	294.6
$\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$	1023	2.05	2.33	−0.52	13.8	184.9

It seems that the larger the Eu concentration, the slower the charge carrier process, likely due to trapping effects by the Eu 4f levels.

Finally, considering the results so far, the $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ samples with $0.4 \leq x \leq 0.6$ were identified as the most promising candidates for water oxidation photoelectrodes. Photocatalytic water oxidation experiments were carried out on $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$. Using pH values below 2 and $\text{Fe}(\text{NO}_3)_3$ as sacrificial agent resulted within 1 h in the decomposition of the material as indicated by the orange color of the suspension. Using a higher pH value of 5.85 and AgNO_3 showed a better materials resistance. However, after 1 h the suspension turned dark grey indicating the deposition of metallic Ag on the material's surface. Finally, at pH 6.54 and NaIO_4 as sacrificial agent 7.5 $\mu\text{mol O}_2$ were produced by 50 mg material within 6 h (s. Figure S8). In all three tested cases the material displayed a significant photocorrosion as expressed by the constant evolution of N_2 from the sample. Such material response is not unusual for bare oxynitride photocatalysts without using protection layers and co-catalysts [38–40] and might be expected from the large τ_{off} times reported in Table 2 pointing to severe hole trapping in the surface-near region of $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$. Further experiments on proper co-catalyst loading and suitable protection layers are required to evaluate the real performance of the material.

The presence of TiN is beneficial to material compaction (s. below), but can hamper the separation of the photoinduced charge carriers. The said samples were prepared with a 20 mol.% excess of Ti precursor and ammonolyzed at 1073 K. The resulting powders were transferred to thin films and analyzed by SPS. None of the TiN-treated samples generated a photovoltage, which is attributed to charge carrier recombination caused by the added TiN.

In order to further analyze the electronical transport properties of $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$, selected samples with $x = 0.2, 0.4, 0.6$, and 0.8 were pressed to pellets as described above. To simulate the “necking” procedure with TiN well-known from the fabrication of Ti-based photoanodes [39, 41, 45], an excess of 20 mol.% Ti precursor was added to the reaction mixture allowing for a homogeneous *in situ* formation of TiN during the compaction process in ammonia. The densities of the samples measured by gas pycnometry after the compaction were in good agreement with the values determined by Rietveld refinements (s. Table S8). Using helium as displacement medium, which is known to penetrate pores down to 1 Å diameter [77], a significant closed porosity of the samples could be excluded. However, control measurements by the Archimedes method in demineralized water revealed the presence of open porosity. This is confirmed by scanning electron microscopy images (s. Figure S9).

The determination of the electronic transport properties of $\text{Eu}_{0.8}\text{Ca}_{0.2}\text{Ti}(\text{O},\text{N})_3$ was hampered by contact problems of the sample. All other samples showed

negative Seebeck coefficients in the entire temperature range (s. Figure S10) confirming the *n*-type semiconducting nature of the samples in agreement with the SPS measurements. The semiconducting behavior can also be inferred from Figure 8, since the electrical resistivity of all samples decreases with increasing temperature. At the same temperature, samples with higher Ca^{2+} contents had lower resistivity. In addition, two areas can be clearly distinguished, namely the extrinsic regime at low temperatures and the intrinsic regime at high temperatures. The extrinsic and intrinsic band gaps of $\text{Eu}_{0.6}\text{Ca}_{0.4}\text{Ti}(\text{O},\text{N})_3$, $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$, and $\text{Eu}_{0.2}\text{Ca}_{0.8}\text{Ti}(\text{O},\text{N})_3$ are calculated according to the Arrhenius equation and summarized in Table 3. In agreement with the 0.5–0.7 eV redshift of the photoonset observed by SPS, the extrinsic conduction points to defect or donor states within the band gap. A donor state (most probably Ti^{3+}) at the bottom of the conduction band as cause for an extrinsic conduction regime has already been reported for pristine $\text{EuTi}(\text{O},\text{N})_3$ [48]. As shown in

Fig. 8: Arrhenius plot of the electrical resistivity of $\text{Eu}_{0.6}\text{Ca}_{0.4}\text{Ti}(\text{O},\text{N})_3$ (black squares), $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ (red circles), and $\text{Eu}_{0.2}\text{Ca}_{0.8}\text{Ti}(\text{O},\text{N})_3$ (blue triangles).

Tab. 3: Summary of electronical band gaps of selected samples $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ derived from temperature-dependent electrical resistivity data.

Material	Intrinsic band gap (eV)	Extrinsic band gap (eV)
$\text{Eu}_{0.6}\text{Ca}_{0.4}\text{Ti}(\text{O},\text{N})_3$	1.84 ± 0.03	0.67 ± 0.03
$\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$	1.32 ± 0.02	0.53 ± 0.01
$\text{Eu}_{0.2}\text{Ca}_{0.8}\text{Ti}(\text{O},\text{N})_3$	1.74 ± 0.04	0.39 ± 0.01

Table 3, the extrinsic band gap decreases with increasing Ca^{2+} content. A similar trend was observed for the respective oxides, for which both the intrinsic and the extrinsic band gaps were reduced with increasing Ca^{2+} substitution [50]. For $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$, the situation is more complex as the intrinsic band gap increases while the extrinsic band gap decreases. Chemical analysis indicates that the decrease of the extrinsic band gap can be ascribed to the enhanced formation of oxygen vacancies (s. Table S5) formed for charge balance purposes when the nitrogen content exceeds the respective Eu content. As a consequence, this forces the simultaneous formation of Ti^{3+} levels expanding the donor levels toward the conduction band and, thus, reducing the extrinsic band gap. The variations of the intrinsic band gaps derived from the electrical resistivity are controlled by several effects: (i) the concentration of $\text{Eu}4f$ and $\text{N}2p$ levels in the valence band, (ii) the degree of distortion of the octahedral network, (iii) the concentration and distribution of TiN, and (iv) the amount of potentially remaining open porosity. Tracing the intrinsic band gap and the electrical resistivity to a common single origin is complicated by the sophisticated interrelations in this system. In the following, we examine the most obvious relationships.

Based on the published electronic band structure of $\text{EuTi}(\text{O},\text{N})_3$ [48] the valence band consists of $\text{Eu}4f$, and hybridized $\text{O}2p$ and $\text{N}2p$ levels, the top part mainly hosting $\text{Eu}4f$ and $\text{N}2p$ levels. Consequently, increasing Ca^{2+} substitution resulted in a dilution of these states and a downwards shift of the valence band edge leading to a widening of the (optical) band gap as observed by DRS (s. Table 1). Reportedly [33, 48, 56], octahedral network tilting resulted in a decrease of the band width of the titanium antibonding levels forming the conduction band. Both effects contributed synergistically to a larger (optical) band gap. In case of the electronic (intrinsic) band gap, this behavior was more difficult to recognize, since it was overlaid by varying concentrations and a potentially deviating distribution of the TiN sintering aid. Besides, an effect of different patterns of open porosity on the electrical resistivity measurements cannot be entirely excluded. Nevertheless, the compositional dependency of the intrinsic band gaps summarized in Table 3 can be explained. $\text{Eu}_{0.6}\text{Ca}_{0.4}\text{Ti}(\text{O},\text{N})_3$ had the largest intrinsic band gap and electrical resistivity within the series of three samples indicating the absence of significant amounts of TiN in agreement with the PXRD data. The value of the intrinsic band gap (s. Table 3) was located well between the optical band gap values of $\text{Eu}_{0.8}\text{Ca}_{0.2}\text{Ti}(\text{O},\text{N})_3$ and $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ powder samples determined by DRS (s. Table S7). Since TiN is a metallic conductor [78], even small impurities could enhance the electrical conductivity and lower the activation energy, which is in accordance with SPS measurement data of powder samples showing the influence of TiN on the charge carriers. The PXRD patterns of $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ and $\text{Eu}_{0.2}\text{Ca}_{0.8}\text{Ti}(\text{O},\text{N})_3$ clearly revealed a TiN secondary phase.

The refined TiN content of the pellets increased from 0.20(6) wt.% to 3.6(3) wt.% for the samples with $x = 0.6$ and $x = 0.8$, respectively. This explains well the decrease of the electrical resistivity with increasing Ca^{2+} content (s. Figure 8). Associated to this, the intrinsic band gaps from electrical resistivity measurements of the samples with $x = 0.6, 0.8$ were smaller than that of the sample with $x = 0.4$ (s. Table 3). An increasing trend as expected from the enhanced octahedral network tilting and the dilution of the $\text{Eu}4f$ and $\text{N}2p$ levels was observed when increasing the calcium content from $x = 0.6$ to $x = 0.8$. This trend agrees with that of the optical band gap, but the obtained intrinsic band gap values were significantly smaller due to the influence of TiN.

Combining the results from PXRD, chemical analysis, SPS, and electrical resistivity measurements with DFT calculation data from literature [48], the following simplified schematic picture of the electronic band structure can be drawn (s. Figure 9): The valence band is composed of $\text{Eu}4f$, and hybridized $\text{O}2p$ and $\text{N}2p$ levels, while the conduction band consists mainly of empty $\text{Ti}3d$ levels.

Fig. 9: Schematic simplified electronic band structure of $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ ($x = 0.4, 0.6, 0.8$). VB = valence band consisting of $\text{Eu}4f$, and hybridized $\text{O}2p$ and $\text{N}2p$ levels. CB = conduction band, mainly consisting of empty $\text{Ti}3d$ levels. E_F = Fermi level. E_g = optical band gap (direct band gap). The calculated electronic band structure of $\text{EuTi}(\text{O},\text{N})_3$ and $\text{Eu}_{1-x}\text{Ca}_x\text{TiO}_{3-\delta}$, respectively, can be found in literature [48–50].

The intrinsic band gap is correlated with the Ca^{2+} content of the sample in such way that a higher Ca^{2+} content results in a larger band gap. This is attributed to a synergetic effect of dilution of the $\text{Eu}4f$ and $\text{N}2p$ states in the valence band and a smaller dispersion of the conduction band caused by the enhanced distortion of the octahedral network. Simultaneously, materials with higher Ca^{2+} content ($x \geq 0.7$) are more susceptible to the formation of Ti^{3+} donor levels below the conduction band originating either from TiN or the intrinsic formation due to oxygen vacancies in $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ for charge balance purposes when the nitrogen content exceeds the europium content of the sample. This leads to broader Ti^{3+} levels reducing the extrinsic band gap with raising Ca^{2+} content. The fact that the electronic (intrinsic) band gaps were always smaller than the optical band gaps for $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ is pointing in agreement with common knowledge [79] to an indirect semiconducting behavior of these materials.

4 Conclusion

The series $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ ($0 \leq x \leq 0.9$) was synthesized by a two-step reaction procedure via ammonolysis of microcrystalline or nanocrystalline oxide precursors in the temperature range of 873 K and 1273 K. Increasing the Ca^{2+} content of the samples increased the tilting of the octahedral network indicated by the enhanced deviation of the Ti–X(1)–Ti and Ti–X(2)–Ti angles from 180° determined by Rietveld refinements of the PXRD patterns. This led to a widening of the optical band gap up to 2.56 eV, but also made the materials more susceptible to the formation of Ti^{3+} levels either as TiN secondary phase or forced by oxygen vacancies. Therefore, a precise adjustment of the ammonolysis temperature is crucial to control the formation of TiN. The presence of a small amount of TiN ($w \leq 4$ wt.%) was identified to be beneficial to the compaction of selected $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ samples. The compaction did not produce measurable amounts of closed porosity, but open porosity was present. These samples enabled the rare investigation of the electrical transport properties of perovskite-type oxynitrides. A negative surface photovoltage and Seebeck coefficient confirmed the *n*-type semiconducting behavior. However, TiN concentrations even below the PXRD detection limit inhibited photovoltage formation by carrier recombination. $\text{Eu}_{0.1}\text{Ca}_{0.9}\text{Ti}(\text{O},\text{N})_3$ synthesized at 978 K showed the fastest carrier transport and the largest photovoltage (-1.20 V) of all samples. Higher Eu contents (e.g. $x = 0.4$) and higher ammonolysis temperatures introduced defects acting as trapping and recombination sites for photoinduced charge carriers. $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ showed a general suitability for water oxidation, but the photocorrosion of the bare material is significant, most probably due to the persistent hole trapping at the surface as

indicated by the large τ_{off} time of up to 486 s. For a conclusive judgement of the photocatalytic performance of $\text{Eu}_{0.4}\text{Ca}_{0.6}\text{Ti}(\text{O},\text{N})_3$ further investigations on protection layers and co-catalysts are required. The before-hand mentioned defect states might be related to Ti^{3+} levels and the internal $\text{Eu}^{2+}(4f^7)/\text{Eu}^{3+}(4f^6)$ redox couple. The electronic band gaps were smaller than the optical band gaps, but still in reasonable agreement, most probably caused by the presence of Ti^{3+} donor states or TiN as sintering aid pointing to an indirect semiconductor. Combining all experimental results allowed the construction of a first schematic electronic band structure model of $\text{Eu}_{1-x}\text{Ca}_x\text{Ti}(\text{O},\text{N})_3$ materials. However, further band structure calculations are required to gain a deeper understanding of the involved interrelations. Overall, the presented approach may be useful for the synthesis of novel visible light-active, transition metal-containing oxynitrides with improved electrical conductivity.

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References

1. R. Marchand, F. Pors, Y. Laurent, *Ann. Chim. Fr.* **16** (1991) 553.
2. E. Günther, R. Hagenmeyer, M. Jansen, *Z. Anorg. Allg. Chem.* **626** (2000) 1519.
3. S. G. Ebbinghaus, H. P. Abicht, R. Dronskowski, T. Müller, A. Reller, A. Weidenkaff, *Prog. Solid State Chem.* **37** (2009) 173.
4. T. Motohashi, Y. Hamade, Y. Masubuchi, T. Takeda, K. Murai, A. Yoshiasa, S. Kikkawa, *Mater. Res. Bull.* **44** (2009) 1899.

5. D. Logvinovich, S. G. Ebbinghaus, A. Reller, I. Marozau, D. Ferri, A. Weidenkaff, Z. Anorg. Allg. Chem. **636** (2010) 905.
6. M. Yang, J. Oró-Solé, J. A. Rodgers, A. Belén Jorge, A. Fuertes, J. P. Attfield, Nat. Chem. **3** (2011) 47.
7. A. Maegli, S. Yoon, E. Otal, L. Karvonen, P. Mandaliev, A. Weidenkaff, J. Solid State Chem. **184** (2011) 929.
8. A. Fuertes, J. Mater. Chem. **22** (2012) 3293.
9. Y. Il Kim, Y. Paik, Solid State Sci. **14** (2012) 580.
10. P. J. Camp, A. Fuertes, J. P. Attfield, J. Am. Chem. Soc. **134** (2012) 6762.
11. A. E. Maegli, T. Hisatomi, E. H. Otal, S. Yoon, S. Pokrant, M. Grätzel, A. Weidenkaff, J. Mater. Chem. **22** (2012) 17906.
12. J. P. Attfield, Cryst. Growth Des. **13** (2013) 4623.
13. M. Jansen, H. P. Letschert, Nature **404** (2000) 980.
14. D. Li, W. Li, C. Fasel, J. Shen, R. Riedel, J. Alloys Compd. **586** (2014) 567.
15. A. E. Maegli, S. Pokrant, T. Hisatomi, M. Trottmann, K. Domen, A. Weidenkaff, J. Phys. Chem. C **118** (2014) 16344.
16. Y. Il Kim, Ceram. Int. **40** (2014) 5275.
17. S. H. Porter, Z. Huang, Z. Cheng, M. Avdeev, Z. Chen, S. Dou, P. M. Woodward, J. Solid State Chem. **226** (2015) 279.
18. Y. Masubuchi, S.-K. Sun, S. Kikkawa, Dalt. Trans. **44** (2015) 10570.
19. D. Chen, D. Habu, Y. Masubuchi, S. Torii, T. Kamiyama, S. Kikkawa, Solid State Sci. **54** (2016) 2.
20. S. Kikkawa, S. Sun, Y. Masubuchi, Y. Nagamine, T. Shibahara, Chem. Mater. **28** (2016) 1312.
21. F. Oehler, S. G. Ebbinghaus, Solid State Sci. **54** (2016) 43.
22. D. Habu, Y. Masubuchi, S. Torii, T. Kamiyama, S. Kikkawa, J. Solid State Chem. **237** (2016) 254.
23. M. Hojamberdiev, M. F. Bekheet, J. N. Hart, J. J. M. Vequizo, A. Yamakata, K. Yubuta, A. Gurlo, M. Hasegawa, K. Domen, K. Teshima, Phys. Chem. Chem. Phys. **19** (2017) 22210.
24. A. Kasahara, K. Nukumizu, G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, J. Phys. Chem. A **106** (2002) 6750.
25. N. Cordes, W. Schnick, Chem. A Eur. J. **23** (2017) 11410.
26. A. Fuertes, Prog. Solid State Chem. **51** (2018) 63.
27. Y.-I. Kim, P. M. Woodward, K. Z. Baba-Kishi, C. W. Tai, Chem. Mater. **16** (2004) 1267.
28. F. Cheviré, F. Tessier, R. Marchand, Eur. J. Inorg. Chem. **2006** (2006) 1223.
29. D. Logvinovich, A. Börger, M. Döbeli, S. G. Ebbinghaus, A. Reller, A. Weidenkaff, Prog. Solid State Chem. **35** (2007) 281.
30. J. Zhao, F. E. Osterloh, J. Phys. Chem. Lett. **5** (2014) 782.
31. A. Jorge Belen, J. Oro-Sole, A. M. Bea, N. Mufti, T. T. M. Palstra, J. A. Rodgers, J. P. Attfield, A. Fuertes, J. Am. Chem. Soc. **130** (2008) 12572.
32. D. Logvinovich, L. Bocher, D. Sheptyakov, R. Figi, S. G. Ebbinghaus, R. Aguiar, M. H. Aguirre, A. Reller, A. Weidenkaff, Solid State Sci. **11** (2009) 1513.
33. M. Widenmeyer, C. Peng, A. Baki, W. Xie, R. Niewa, A. Weidenkaff, Solid State Sci. **54** (2016) 7.
34. C. Bubeck, M. Widenmeyer, G. Richter, M. Coduri, S. Yoon, A. Weidenkaff, Commun. Chem. **2** (2019) 134.

35. S. Yoon, A. E. Maegli, L. Karvonen, S. K. Matam, A. Shkabko, S. Riegg, T. Großmann, S. G. Ebbinghaus, S. Pokrant, A. Weidenkaff, *J. Solid State Chem.* **206** (2013) 226.
36. S. Yoon, K. Son, S. G. Ebbinghaus, M. Widenmeyer, A. Weidenkaff, *J. Alloys Compd.* **749** (2018) 628.
37. Y. Moriya, T. Takata, K. Domen, *Coord. Chem. Rev.* **257** (2013) 1957.
38. K. Kawashima, M. Hojamberdiev, H. Wagata, K. Yubuta, J. J. M. Vequizo, A. Yamakata, S. Oishi, K. Domen, K. Teshima, *J. Phys. Chem. C* **119** (2015) 15896.
39. S. Landsmann, A. E. Maegli, M. Trottmann, C. Battaglia, A. Weidenkaff, S. Pokrant, *ChemSusChem* **8** (2015) 3451.
40. S. Landsmann, Y. Surace, M. Trottmann, S. Dilger, A. Weidenkaff, S. Pokrant, *ACS Appl. Mater. Interfaces* **8** (2016) 12149.
41. M. Pichler, D. Pergolesi, S. Landsmann, V. Chawla, J. Michler, M. Döbeli, A. Wokaun, T. Lippert, *Appl. Surf. Sci.* **369** (2016) 67.
42. L. Wan, F.-Q. Xiong, Y. Li, T. Thomas, R. Che, M. Yang, *Mater. Lett.* **188** (2017) 212.
43. M. Hojamberdiev, M. F. Bekheet, E. Zahedi, H. Wagata, Y. Kamei, K. Yubuta, A. Gurlo, N. Matsushita, K. Domen, K. Teshima, *Cryst. Growth Des.* **16** (2016) 2302.
44. J. Fu, S. E. Skrabalak, *Angew. Chemie* **56** (2017) 14357.
45. C. M. Leroy, A. E. Maegli, K. Sivula, T. Hisatomi, N. Xanthopoulos, E. H. Otal, S. Yoon, A. Weidenkaff, R. Sanjines, M. Grätzel, *Chem. Commun.* **48** (2012) 820.
46. J. H. Lee, X. Ke, N. J. Podraza, L. Fitting Kourkoutis, T. Heeg, M. Roeckerath, J. W. Freeland, C. J. Fennie, J. Schubert, D. A. Muller, P. Schiffer, D. G. Schlom, *Appl. Phys. Lett.* **94** (2009) 212509.
47. T. Kolodiazhnyi, M. Valant, J. R. Williams, M. Bugnet, G. A. Botton, N. Ohashi, Y. Sakka, *J. Appl. Phys.* **112** (2012) 083719.
48. L. Sagarna, K. Z. Rushchanskii, A. E. Maegli, S. Yoon, S. Populoh, A. Shkabko, S. Pokrant, M. Lezaic, R. Waser, A. Weidenkaff, *J. Appl. Phys.* **114** (2013) 033701.
49. K. Jiang, R. Zhao, P. Zhang, Q. Deng, J. Zhang, W. Li, Z. Hu, H. Yang, J. Chu, *Phys. Chem. Chem. Phys.* **17** (2015) 31618.
50. X. Xiao, M. Widenmeyer, K. Mueller, M. Scavini, S. Checchia, C. Castellano, D. Ma, S. Yoon, W. Xie, U. Starke, K. Zakharchuk, A. Kovalevsky, *Mater. Today Phys.* **7** (2018) 96.
51. R. Mikita, T. Aharen, T. Yamamoto, F. Takeiri, T. Ya, W. Yoshimune, K. Fujita, S. Yoshida, K. Tanaka, D. Batuk, A. M. Abakumov, C. M. Brown, Y. Kobayashi, H. Kageyama, *J. Am. Chem. Soc.* **138** (2016) 3211.
52. R. D. Shannon, *Acta Crystallogr. Sect. A* **32** (1976) 751.
53. X. Liu, R. C. Liebermann, *Phys. Chem. Miner.* **20** (1993) 171.
54. A. Bohre, K. Avasthi, O. P. Shrivata, *Cryst Rep* **59** (2014) 944.
55. X. Xiao, M. Widenmeyer, W. Xie, T. Zou, S. Yoon, M. Scavini, S. Checchia, Z. Zhong, P. Hansmann, S. Kilper, A. Kovalevsky, A. Weidenkaff, *Phys. Chem. Chem. Phys.* **19** (2017) 13469.
56. D. Logvinovich, A. Weidenkaff, A. Reller, A. Rachel, S. G. Ebbinghaus, R. Aguiar, *Dye. Pigment.* **76** (2006) 70.
57. L. Kronik, Y. Shapira, *Surf. Sci. Rep.* **37** (1999) 1.
58. Y. Yang, J. Wang, J. Zhao, B. A. Nail, X. Yuan, Y. Guo, F. E. Osterloh, *ACS Appl. Mater. Interfaces* **7** (2015) 5959.
59. G. Sharma, Z. Zhao, P. Sarker, B. A. Nail, J. Wang, M. N. Huda, F. E. Osterloh, *J. Mater. Chem. A* **4** (2016) 2936.

60. M. Kodera, J. Wang, B. A. Nail, J. Liu, H. Urabe, T. Hisatomi, M. Katayama, T. Minegishi, F. E. Osterloh, K. Domen, *Chem. Phys. Lett.* **683** (2017) 140.
61. X. Ma, X. Cui, Z. Zhao, M. A. Melo, E. J. Roberts, F. E. Osterloh, *J. Mater. Chem. A* **6** (2018) 5774.
62. J. Rodriguez-Carvajal, FullProf2.k, version 5.30 (2012).
63. G. Kortüm, W. Braun, G. Herzog, *Angew. Chem. Int. Ed.* **2** (1963) 333.
64. J. A. Dean, *Handbook of Chemistry*, McGra-Hill Inc., New York (1999).
65. R. L. Cook, A. F. Sammells, *Solid State Ionics* **45** (1991) 311.
66. X. Wang, T. Wu, M. R. Zachariah, *J. Phys. Chem. C* **121** (2017) 147.
67. A. E. Maegli, E. H. Otal, T. Hisatomi, S. Yoon, C. M. Leroy, N. Schäuble, Y. Lu, M. Grätzel, A. Weidenkaff, *Energy Procedia* **22** (2011) 61.
68. A. E. Maegli, L. Sagarna, S. Populoh, B. Penkala, E. H. Otal, A. Weidenkaff, *J. Solid State Chem.* **211** (2014) 106.
69. P. Thiel, S. Populoh, S. Yoon, G. Saucke, K. Rubenis, A. Weidenkaff, *J. Phys. Chem. C* **119** (2015) 21860.
70. H. C. Gatos, J. Lagowski, *J. Vac. Sci. Technol.* **10** (1973) 130.
71. L. Kronik, Y. Shapira, *Surf. Interface Anal.* **31** (2001) 954.
72. D. Heredia, L. Otero, M. Gervaldo, F. Fungo, T. Dittrich, C.-Y. Lin, L.-C. Chi, F.-C. Fang, K.-T. Wong, *Thin Solid Films* **527** (2013) 175.
73. T. Dittrich, A. Gonzáles, T. Rada, T. Rissom, E. Zillner, S. Sadewasser, M. Lux-Steiner, *Thin Solid Films* **535** (2013) 357.
74. M. A. Melo, Z. Wu, B. A. Nail, A. T. De Denko, A. F. Nogueira, F. E. Osterloh, *Nano Lett.* **18** (2018) 805.
75. J. Zhao, B. A. Nail, M. A. Holmes, F. E. Osterloh, *J. Phys. Chem. Lett.* **7** (2016) 3335.
76. J. Wang, J. Zhao, F. E. Osterloh, *Energy Environ. Sci.* **8** (2015) 2970.
77. Micromeritics, ACCUPYC II Gas Displacement Pycnometry System (2015).
78. W. S. Williams, *J. Matter* **49** (1997) 38.
79. J. Singleton, *Band Theory and Electronic Properties of Solids*, Oxford University Press Inc., New York (2001).

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