

# Electronic Structure of Quaternary $\text{In}_{1-x-y}\text{Sc}_x\text{Y}_y\text{N}$ Materials

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Received: 13.10.2021 & Accepted: 22.11.2021

Doi: [10.12693/APhysPolA.140.463](https://doi.org/10.12693/APhysPolA.140.463)

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Structural and electronic properties of quaternary alloys of indium and rare earth element (Sc, Y) nitrides have been studied by *ab initio* calculations. Equilibrium structures were obtained within the generalized gradient approximation, whereas fully relativistic band structures were calculated with the use of the modified Becke–Johnson potential. The introduction of rare earth ions into the InN host material leads to an increase of a unit cell volume. The codoping with Sc and Y is expected to minimize the lattice mismatch in the quaternary systems. A relatively wide range of band gaps provided by  $\text{In}_{1-x-y}\text{Sc}_x\text{Y}_y\text{N}$ , from 0.7 up to 2.4 eV, may be desired in some optoelectronic devices. The rapid increase of the band gap in such quaternary nitrides is related to the strong chemical pressure caused by big ionic radii of scandium and yttrium.

topics: electronic structure, DFT, nitride alloys

## 1. Introduction

Indium nitride is a semiconductor with a narrow band gap ( $E_g$ ) of 0.69 eV [1, 2] that can be used in optoelectronic devices operating in the infrared region. However, the range of  $E_g$  available in group III nitride materials is exceptionally wide [3]. The most common applications of In-based nitrides are based on ternary  $\text{In}_{1-x}\text{Ga}_x\text{N}$  and  $\text{In}_{1-x}\text{Al}_x\text{N}$  alloys, widely used in light emitting diodes. Solid solutions of InN, GaN and AlN exhibit a strong band gap bowing [4].

Further engineering of the band gap in group III nitride materials can be achieved with the rare earth (RE) element doping. Experimental studies for  $\text{Ga}_{1-x}\text{Sc}_x\text{N}$  [4–6],  $\text{Al}_{1-x}\text{Sc}_x\text{N}$  [7–9], and  $\text{Al}_{1-x}\text{Y}_x\text{N}$  [10] alloys showed a rather linear decrease in  $E_g$  with an increasing RE content, and high quality wurtzite thin films of such materials were obtained for compositions with  $x < 0.5$ . Furthermore, the local crystal structures of the systems are strongly affected by the presence of rare earth ions, i.e., a flattening of hexagonal atomic layers was reported for  $\text{Ga}_{1-x}\text{Sc}_x\text{N}$  [5]. This phenomenon is related to the metastable BN type phase in rare earth nitride (REN) systems [11, 12] and was extensively investigated in recent DFT-based studies for ternary alloys of group III and RE nitrides [13, 14].

In spite of the small lattice mismatch between InN and REN materials there are no experimental reports on RE-doped InN up to now. The introduction of RE ions in InN is expected to increase unit cell volume and widen  $E_g$  [14]. However, the

relatively large ionic radius of yttrium may lead to undesirable changes in the crystal structure (a rapid decrease of the  $c/a$  ratio). This effect is less pronounced in Sc-doped InN systems [14].

In this work, the structural and electronic properties of quaternary alloys of InN, ScN, and YN are investigated from the first principles in order to predict novel nitride materials for applications in optoelectronics. The equilibrium structures were found within the generalized gradient approximation (GGA). The band structures were obtained with the fully relativistic MBJGGA calculations. The effects of co-doping with Sc and Y ions on the electronic structure of InN are examined and discussed.

## 2. Computational details

The VASP package was used in the calculations [15, 16] with the plane augmented wave approach (PAW [17]). The GGA and MBJGGA parameterizations of the exchange–correlation were selected [18, 19]. The MBJGGA approach is the Tran–Blaha modified Becke–Johnson potential for insulators and semiconductors combined with the GGA correlation term. The plane-wave energy cutoff of 500 eV,  $6 \times 6 \times 6$   $\mathbf{k}$ -point mesh, and spin–orbit coupling were employed. The geometry of  $2 \times 2 \times 2$  wurtzite supercells was fully relaxed due to forces and stress. As homogeneous models of solid solutions as possible were selected, as depicted in Fig. 1 for  $\text{In}_{0.875}\text{Sc}_{0.0625}\text{Y}_{0.0625}\text{N}$ . The alloy compositions considered in this work are consistent

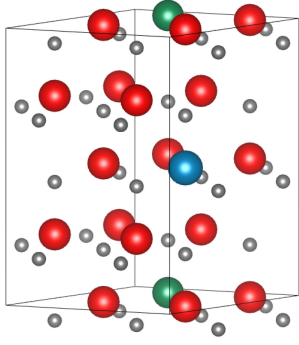


Fig. 1. The wurtzite supercell of the ternary alloy  $\text{In}_{0.875}\text{Sc}_{0.0625}\text{Y}_{0.0625}\text{N}$ . The In, Sc, Y, and N ions are marked with red, green, blue, and gray color, respectively.

with the conclusions of previous DFT-based studies [13, 14] which showed that ternary wurtzite-type materials are expected to be stable for RE contents less than 0.5.

### 3. Results and discussion

The GGA-derived lattice parameter,  $a = 3.578 \text{ \AA}$ , and the  $c/a$  ratio of 1.619, obtained for the parent InN material are slightly overestimated with respect to the experimental data  $3.544 \text{ \AA}$  and 1.613, respectively [20]. Similar results were reported in previous GGA studies [14, 21]. The doping with RE ions results in a strong increase of the in-plane lattice parameters of the alloys, as presented in Fig. 2. This effect is clearly related to the increasing yttrium content in the materials. The introduction of Sc ions leads to an opposite evolution of the unit cell, i.e. the lattice parameters  $a$  of systems with high  $x$  are reduced. The lattice mismatch with respect to InN, which is caused by yttrium, can therefore be balanced with the addition of scandium in quaternary systems.

The design of quaternary alloys proposed in this work is also favourable for the stabilization of the  $c/a$  ratio in mixed group III and RE nitrides. Namely, as depicted in Fig. 3, the decrease of  $c/a$  is balanced with increasing Sc contents. The flattening of the wurtzite structure is clearly pronounced in the ternary  $\text{In}_{1-y}\text{Y}_y\text{N}$  systems (the wurtzite  $\text{In}_{0.5}\text{Y}_{0.5}\text{N}$  is expected to be unstable), whereas the structure of quaternary materials can be affected in less extent.

The MBJGGA-derived band gap of InN,  $E_g = 0.70 \text{ eV}$ , is in excellent agreement with the experimental data [1], whereas the previous MBJLDA calculations resulted in an overestimated  $E_g$  for this compound [22, 23]. It is worth recalling that the HSE approach yields slightly underestimated band gaps of group III nitrides ( $E_g = 0.63 \text{ eV}$  for InN [21]), which can be tuned with the increased amount of exact exchange in the exchange-correlation functional. The MBJGGA approach

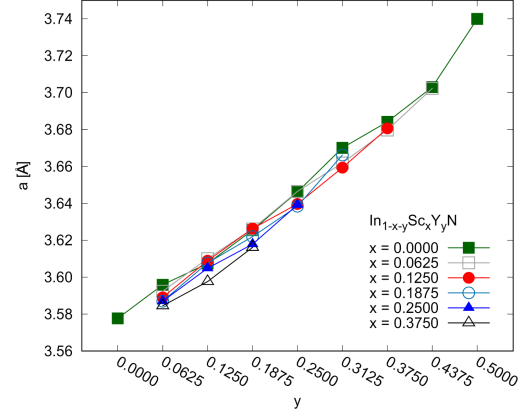


Fig. 2. The lattice parameters  $a$  calculated with GGA for wurtzite  $\text{In}_{1-x-y}\text{Sc}_x\text{Y}_y\text{N}$  materials.

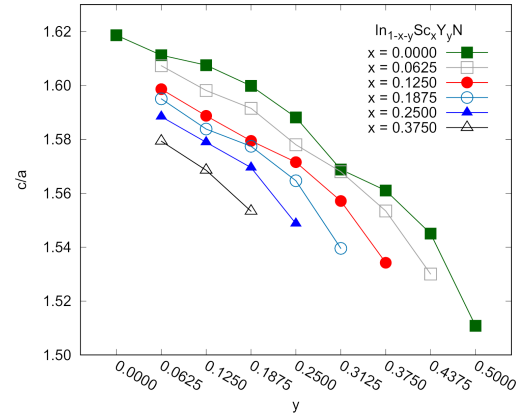


Fig. 3. The ratio of  $c/a$  (GGA) of wurtzite  $\text{In}_{1-x-y}\text{Sc}_x\text{Y}_y\text{N}$  alloys.

seems to be the most suitable one for investigations of the electronic structure of InN-based materials.

The band gaps predicted for systems studied in this work are depicted in Fig. 4. It is expected that the ternary  $\text{In}_{1-y}\text{Y}_y\text{N}$  alloys exhibit a rapid increase of  $E_g$  as a function of yttrium content, which has been discussed in a recent study [14]. As seen in Fig. 4, the dependence is linear with a slope modification at  $y \approx 0.31$ . Interestingly, the influence of Y ions on  $E_g$  in InN is much stronger than the analogous effect of Ga in the well-known  $\text{In}_{1-x}\text{Ga}_x\text{N}$  systems [2, 21]. The introduction of Sc ions in the  $\text{In}_{1-y}\text{Y}_y\text{N}$  materials leads to a further widening of  $E_g$ , e.g., the  $\text{In}_{0.750}\text{Sc}_{0.125}\text{Y}_{0.125}\text{N}$  system may exhibit  $E_g = 1.69 \text{ eV}$ . Although the ranges of reasonable  $x$  and  $y$  in  $\text{In}_{1-x-y}\text{Sc}_x\text{Y}_y\text{N}$  alloys are limited due to the robustness of the rock salt phase in systems with In content less than 0.5, one may consider many wurtzite materials with band gaps from 0.7 up to 2.4 eV.

It is worth highlighting that the codoping with Sc and Y in InN is suitable not only for tuning of the lattice mismatch but also leads to the strong

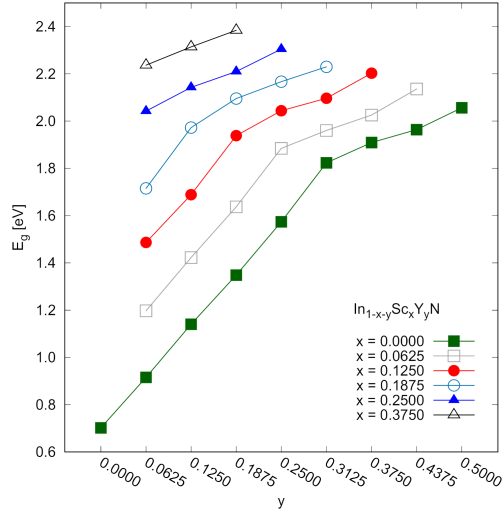


Fig. 4. The band gaps (MBJGGA) of quaternary  $\text{In}_{1-x-y}\text{Sc}_x\text{Y}_y\text{N}$  systems.

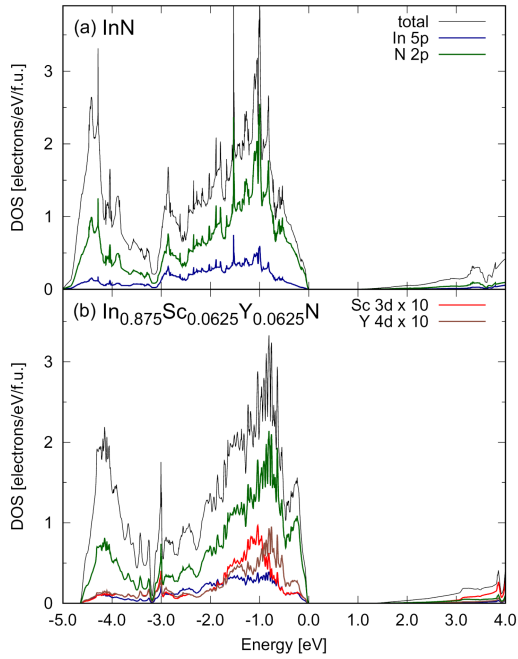


Fig. 5. The density of states (DOS) plots calculated (MBJLDA) for  $\text{InN}$  (a) and  $\text{In}_{0.875}\text{Sc}_{0.0625}\text{Y}_{0.0625}\text{N}$  (b). Note that the RE  $d$ -type contributions are magnified by 10.

widening of  $E_g$ , which could not be obtained in any ternary alloys from the set of ions considered here [14]. The origin of this phenomenon could be connected with some characteristic electronic features of the materials, which are usually discussed on the basis of the density of states (DOS). As seen in Fig. 5a, the total DOS in the valence region of  $\text{InN}$  is dominated by the N  $2p$  states with a minor In  $5p$  contributions. The maximums of additional  $d$ -electron peaks of the RE ions in the quaternary alloys, depicted in Fig. 5b, are centered at about 1.1

and 0.8 eV below VBM for Sc and Y, respectively. The tail-like shape of the conduction band region is characteristic of nitride compounds. The contributions of unoccupied  $d$ -type states coming from RE ions are located well above the conduction band minimums (CBM) of ternary and quaternary materials.

Considering the relatively small amplitudes of these dopant states and their location with respect to VBM and CBM of a host  $\text{InN}$  system, the rapid increase of  $E_g$  in quaternary alloys of  $\text{InN}$  and RE  $\text{N}$  semiconductors is related to certain chemical pressure present in these materials. Namely, the In-based nitrides exhibit positive  $dE_g/dP$  [24]. The local stress caused by significantly bigger RE ions than indium is expected to be the main cause of the rapid increase of  $E_g$  in the quaternary alloys studied in this work.

#### 4. Conclusions

The structural properties of quaternary  $\text{In}_{1-x-y}\text{Sc}_x\text{Y}_y\text{N}$  nitrides predicted in this work based on the DFT calculations suggest that the codoping with Sc and Y may be a reasonable approach to minimize lattice mismatch in RE-doped  $\text{InN}$  systems. In this case, the decrease of  $c/a$  ratio, which is undesired in wurtzite materials, is also diminished. The quaternary  $\text{In}_{1-x-y}\text{Sc}_x\text{Y}_y\text{N}$  alloys are expected to exhibit wider band gaps than those of ternary solid solutions of  $\text{ScN}$ ,  $\text{YN}$  and  $\text{InN}$ . The wide range of available  $E_g$  (from 0.7 up to 2.2 eV) calculated with the MBJGGA approach for the systems studied here indicates potential applications of such materials in optoelectronic devices. The findings presented in this work should encourage further experimental investigations of electronic structures of RE doped group III nitrides.

#### Acknowledgments

This work was supported by the National Science Centre (Poland) under research Grant no. 2017/26/D/ST3/00447. Calculations were performed in Wroclaw Center for Networking and Supercomputing (Project no. 158).

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