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Stability and thermal expansion of InN: An X-ray diffraction study

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Thin films built from binary IIIV nitrides or from their solid solutions are basic components of modern optoelectronic devices. In particular, indium nitride is a component suitable for high-speed electronics and solar cells. Experimental data on the bulk nitride material behaviour under specific thermal conditions (e.g., on variation of its stability, resistance to oxidation, thermal expansion coefficient with temperature) provide a valuable basic information needed for design and development of such devices. The properties such as decomposition temperature, oxidation rate at elevated temperatures, and thermal expansion are of importance for technologies of growth of low-dimensional structures. The current knowledge of thermal properties [1–3] may require an extension through studies in neutral or oxidizing environment in broad temperature ranges. The aim of the present work is to present selected experimentally determined temperature-dependent properties (thermal decomposition, interaction with air, thermal expansion) and discuss them on the basis of existing literature data.

Polycrystalline indium nitride samples differing by grain size were sealed in capillaries filled with air and in argon, and then studied by X-ray diffraction in a broad temperature range. High-resolution powder diffractometer at the B2 beamline (DORIS-III, Hasylab, DESY) equipped in a position-sensitive detector ensured collection of data with excellent counting statistics. The X-ray diffraction experiments were conducted at increasing temperatures using a step of 50 K or less; the experiments were stopped when the full decomposition of InN was concluded. High-resolution electron microscopy was used for determination of the microstructure and crystallite size. The structures of InN and minority phases as well as those of the oxidation products were refined using the Rietveld method. The obtained results demonstrate that the decomposition is, as expected, much faster for the sample composed of small grains. The oxide formation, observed when heating indium nitride in air, is attributed to oxidation of the nitride (at moderate temperatures) or to interaction of oxygen with indium vapour (at high temperatures). Thermal expansion was determined from the lattice parameters variation between 22 and 900 K. In this range, the unit-cell volume increases from 61.78 to 62.5 Å³, whereas the thermal expansion coefficient, α_v , increases from 0 to $19 \times 10^{-6} \text{ K}^{-1}$.

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A curious case of hexahydroxytriphenylene

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The D3h symmetry molecule 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) has been an attractive building block for covalent organic frameworks (COFs) [1] and has found use as a mesogen unit in discotic liquid crystals [2]. In the current study the crystal structure of HHTP*4H₂O has been investigated.

Various single crystal x-ray diffraction (SCXRD) measurements performed at different temperatures yielded vital information about the structure and structural changes of the crystals. The as synthesised crystals illustrate the π -stacking motif common to triphenylene systems: the HHTP triphenylene cores assemble in columnar stacks, arranged in a distorted hexagonal array. The solvent water molecules reside in the pores between the stacks and hence an extensive three-dimensional hydrogen bonding network is created. This results in parallel corrugated two-dimensional sheets across the (b,c)-plane.

Our hypothesis is that upon heating and over time the crystals lose the solvate water molecules, resulting in a mixture of phases. Correlating powder x-ray diffraction (PXRD) data with SCXRD data, we can confirm that structural changes do indeed take place over time. It can further be seen that when a sample was left to stand in air for a number of days a phase transition started to occur.

We have taken the first steps to understand this fascinating system and are in the process of finding out more about the structural changes happening upon dehydration.

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Growth, composition, structure and optical properties of ZnO crystals

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Zinc oxide (ZnO) has a great potential in modern opto-, acousto- and microelectronic applications such as semiconductor lighting, piezoelectric transducers and so on. Crystal properties depend on the type and the concentration of the defects, in particular, point defects and their associates. However, the data concerning this topic is almost absent in the literature.

The aim of this work is to establish the relationship between composition, structural peculiarities and perfection, color, optical and electrical characteristics of ZnO crystals.

A series of green (in particular, ZnO1) and light-green (in particular, ZnO2) crystals were grown by the hydrothermal technique combined with a Pt inner container in an aqueous solution of the mineralizers 4M(KOH) + 1M(LiOH) + 0.1M(NH₄OH) by the $t = 330\text{--}350^\circ\text{C}$ and the $P = 30\text{--}50 \text{ MPa}$.

ZnO has the wurtzite structure (sp. gr. P6₃mc, Z=2) where each anion is surrounded by four cations at the corners of a trigonal

pyramid, and vice versa. According to the X-ray powder diffraction data (HZG-4, Ni – filter, CuK α , diffracted beam; exposure time per frame, 15 s; scan step, 0.02°) and X-ray single crystals study (CAD-4, AgK α , ω scan mode) there are an additional reflections related to sp. gr. P3. ZnO1 and ZnO2 crystals have a $[\text{Zn}(1)_{0.500}(\text{Zn}(2)_{0.475(5)0.025})\text{Zn}_{0.015(5)(i)}[(\text{O}(1)_{0.490(6)0.010})\text{O}(2)_{0.500}]$ and $[(\text{Zn}(1)_{0.465(6)0.035})\text{Zn}(2)_{0.500}]\text{Zn}_{0.035(6)(i)}(\text{O}(1)_{0.500})(\text{O}(2)_{0.500})$ refined compositions, respectively. The compositions are in good agreement with the results of X-ray microanalysis (INCA Penta FETx 3). Zinc and oxygen atoms occupy two positions Zn(1), Zn(2) and O(1), O(2) both completely, and partially. Besides, the presence of different quantity of interstitials atoms – Zn_i in the structures of ZnO1 и ZnO2 was found. The alternation of full filled and partially filled Zn and O «layers» in the ZnO structure leads to a symmetry decrease in the local area of the crystal (from sp. gr. P6₃mc to sp. gr. P3).

Due to the fact that X-ray microanalysis did not reveal the presence of impurity atoms and the compositions of green and light green samples differ only in the oxygen content, it can be assumed that the color of ZnO crystals is associated with the oxygen vacancies content: a decrease of oxygen vacancies leads to discoloration of the ZnO crystals. In transmission spectra («Specord-M40») of ZnO two bands are observed: ~445 μm (ZnO1 and ZnO2) и ~625 μm (ZnO1) which correspond to oxygen vacancies - V_O^{••} and color of the crystals, respectively. The color of crystals can be ascribed to a (V_O^{••},ne)^x associate formation, namely centre coloration.

The relationship between the oxygen vacancies content and the structural perfection (diffractometer D8Discover: CuK α ; Ge (002)) of the crystals has been found: the light-green sample is characterized by the lower values of the half-width of the Bragg peak 0002 (28.8° for ZnO1 with (Zn_{0.975 0.025})Zn_{i(0.015)}(O_{0.990 0.010}) general composition and 22.4° for ZnO2 with (Zn_{0.965 0.035})Zn_{i(0.035)}O one). Moreover, the resistivity (ρ) and activation energy (E_a) are higher for the light-green sample ($\rho = 1.5(1) \cdot 10^8$ Ohm-cm, E_a = 0.51(9) eV) than that for the green sample ($\rho = 1.6(1) \cdot 10^7$ Ohm-cm, E_a = 0.38(9) eV).

Keywords: X-ray_study, defects, color

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Defect determination in epitaxial a-plane GaN Layers

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The technological application of (0001), i.e., c-oriented GaN is complicated by the piezoelectric effect along the [0001] direction and non-polar GaN thin films overcome this problem. However, this type of material possesses a large number of defects, especially stacking faults (SF) so that a reliable method for the determination of the defect densities is therefore of large importance.

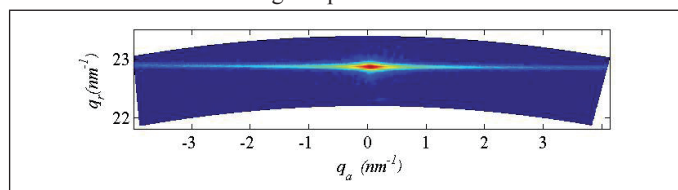


Fig.1. Example of the reciprocal space map of x-ray diffuse scattering measured in the symmetric non-coplanar 10-10 diffraction from an a-GaN epitaxial layer. The axis q_a and q_r are parallel to the sample surface and to the (inclined) diffraction vector, respectively.

We investigated non-polar a-plane oriented GaN epitaxial layers with the (11-20) surface orientation. In these layers, two types of SFs

occur with the displacement vectors $R = 1/6(20-23)$ and $1/3(1-100)$. If $g \cdot R \neq n$ (g is the diffraction vector, n is an integer), the diffuse x-ray scattering from the SFs has the form of [0001]-oriented streaks [1] perpendicular to the fault planes. We have measured the streaks in symmetric non-coplanar diffractions 10-10, 20-20 and 30-30, using a high-resolution x-ray diffraction setup in a series of a-GaN epitaxial layers with various densities of stacking faults (Fig. 1).

We compared the measured intensity distributions along the streaks with simulations supposing a random Markov-like sequence of stacking faults and kinematical approximation; from the comparison we determined the prevailing displacement vector R of the SFs and the fault density.

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High resolution x-ray diffraction analysis of AlGaSb/GaSb

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GaSb single crystals are the ideal substrates for the growth of InGaAsSb, AlGaAsSb, AlGaAs and AlGaSb heterostructures to fabricate optoelectronic devices. GaSb surfaces are highly reactive to oxidation, the oxides grown on their surface have poor conductivity ($\sim 10^{-2} \Omega^{-1} \text{cm}^{-1}$) and it produces high surface leak currents. Using the liquid phase epitaxy (LPE) technique under supercooling conditions we have grown Al_xGa_{1-x}Sb layers doped with tellurium to (100) on n-GaSb (with $0.05 \leq x \leq 0.2$). Using Raman spectroscopy we characterized the structural quality. The Raman spectra show two main peaks located about 224 and 234 cm^{-1} , which were deconvoluted by four Lorentzians. In order to assign the peaks use is made of the random-element isodisplacement (REI) model. Comparison of the experimental results with the values obtained by REI model allows us to confirm that the bands correspond to the LO-like and TO-like of the binary compounds, GaSb. High-resolution X-ray diffraction (HRXRD) has been used to characterize these structures. The out of plane lattice parameter, was estimated directly from the symmetrical diffraction for (001) alloys. These results show that all the layers are relaxed.

Liquid phase epitaxy (LPE) growth was carried out in a single-zone isothermal furnace in hydrogen using the horizontal sliding boat technique. The boat was made from high purity graphite, Al_xGa_{1-x}Sb, were grown nominally lattice-matched to vicinal (100) n-GaSb substrate at a temperature of 673 K. Raman scattering experiments were performed at room temperature using 6328 Å line of a He-Ne laser at normal incidence for excitation. The nominal laser power used in these measurements was 20 mW. Structural characterization of the samples is carried out by means of HRXRD in a Bruker D8 Discover diffractometer, parallel beam geometry and monochromator of gobe mirror, CuK α radiation, 1.5406 Å operated at 40kV and 40mW, in the range of $20^\circ < 2\theta < 80^\circ$ by step of 0.02°.

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