



Influence of various annealing atmospheres on excitonic and defect luminescence properties of single-crystal ZnO

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CONFERENCE

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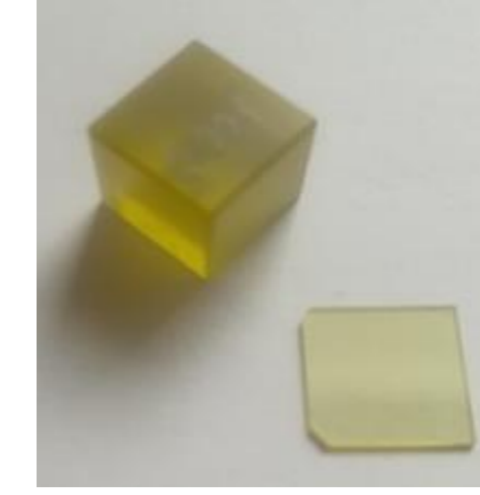
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ZnO is one of the most promising candidates for photocatalytic and antibacterial applications because of its interesting combination of optical, electrical and magnetic properties. Among the most important properties of ZnO are wide direct bandgap (3.37 eV), large exciton binding energy (~60 meV – intense near-band-edge NBE excitonic emission at room and higher temperatures), wide spectral transparency, possibility of band-gap engineering, many special effects (e.g., piezoelectric, pyroelectric, electrooptic etc.), low cost, high chemical stability, high biocompatibility, low toxicity and good eco-friendly characteristics [1,4]. In our research we mainly focus on ion implantation of rare-earth (RE) ions into ZnO. However, the problem is the rigid ZnO structure, in which it is not relatively convenient to place various RE without the emergence of defects [5-7]. The resulting extrinsic defects, together with the intrinsic defects significantly affect the mentioned monitored properties. Therefore in this contribution we focus on the connection between defects and used conditions of annealing on the resulting luminescence properties. We carried out annealing in vacuum, argon and oxygen atmospheres. We have also used 3 different crystallographic cuts of ZnO single crystal in order to investigate the influence of the crystallographic orientation on the defects and luminescence.

EXPERIMENTS

Substrates

- Single crystalline <0001>, <11-20>, <10-10> zinc oxide (ZnO) wafers



Annealing

- Temperature: 600 °C
- Atmospheres: Oxygen, Vacuum, Argon

MEASUREMENTS

- Photoluminescence** measurements were performed on a HORIBA Jobin Yvon Fluorolog®-3 Extreme spectrometer using FluorEssence™3 software. The spectra were collected at room temperature within the range of 250–1000 nm for visible and near-infrared regions (VIS-NIR).
- Raman measurements** were performed on a DXR Raman Microscope spectrometer (Thermo Scientific) equipped with a confocal Olympus microscope. A solid-state Nd:YAG laser (wavelength of 532 nm) was used for the Raman spectroscopy measurements.

Various crystallographic cuts of ZnO:

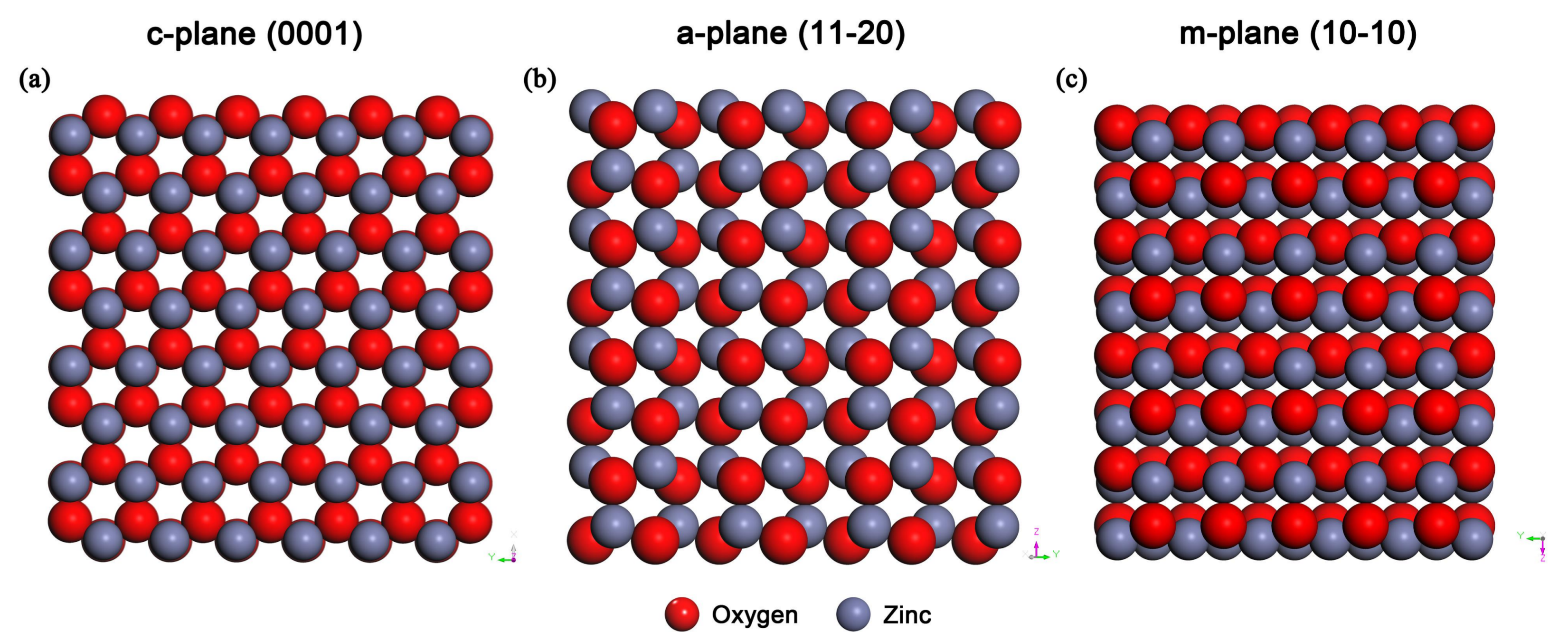
Zinc oxide (ZnO) single-crystal:

Structure

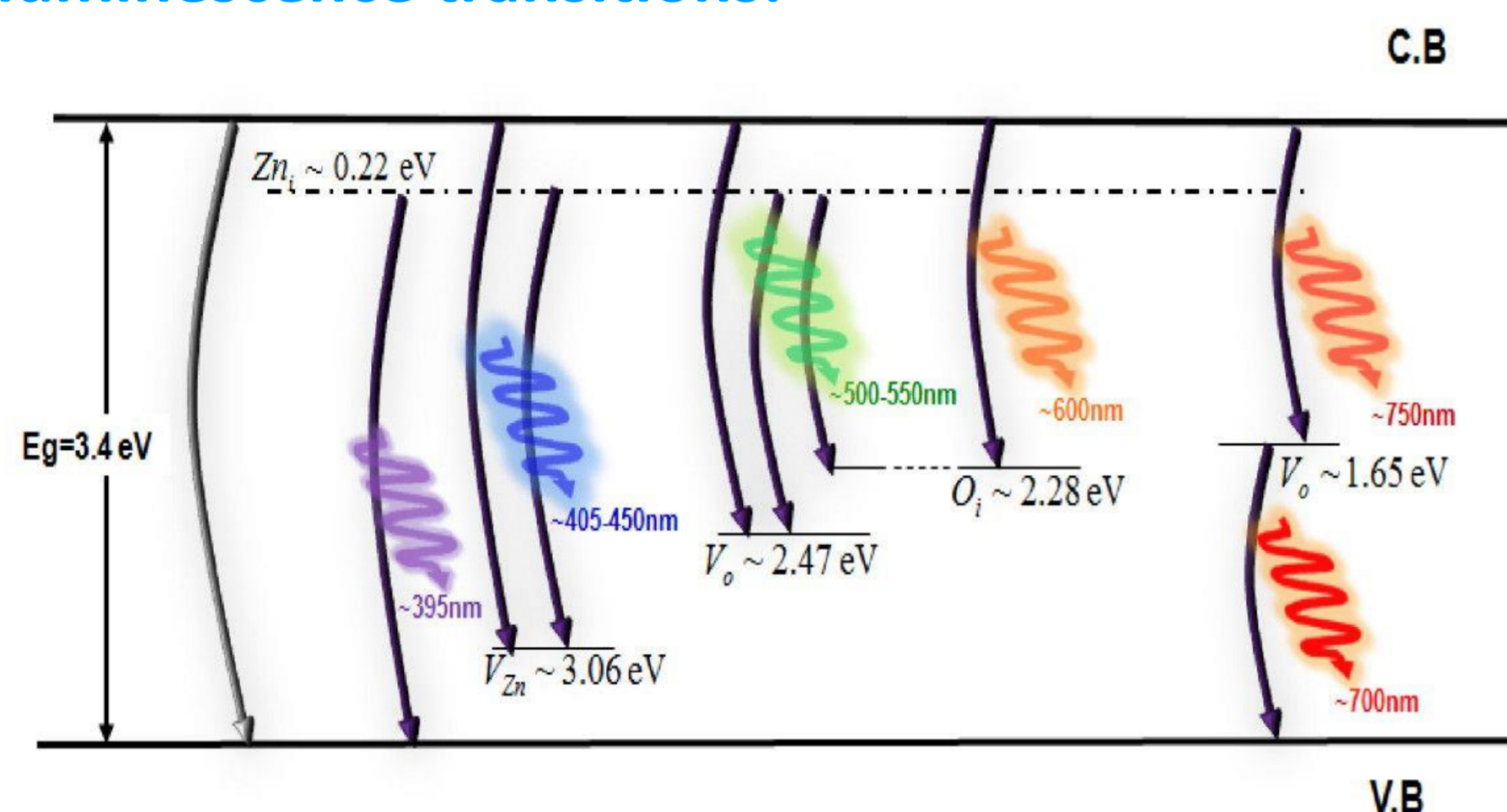
Crystal system: Hexagonal
Space group: P6₃mc (no. 186)
Density: 5.675 g/cm³
Melting point: ~ 1969 °C (>1300°C at p_{atm} decompose)
Refractive index: n_o = 1.989 @ 633 nm
n_e = 2.005 @ 633 nm

Special properties (effects)

Pyroelectric
Acoustooptic
Electrooptic
Piezoelectric
Wide bandgap ~ 3.3 eV
Birefringence (uniaxial)
Optical nonlinearity



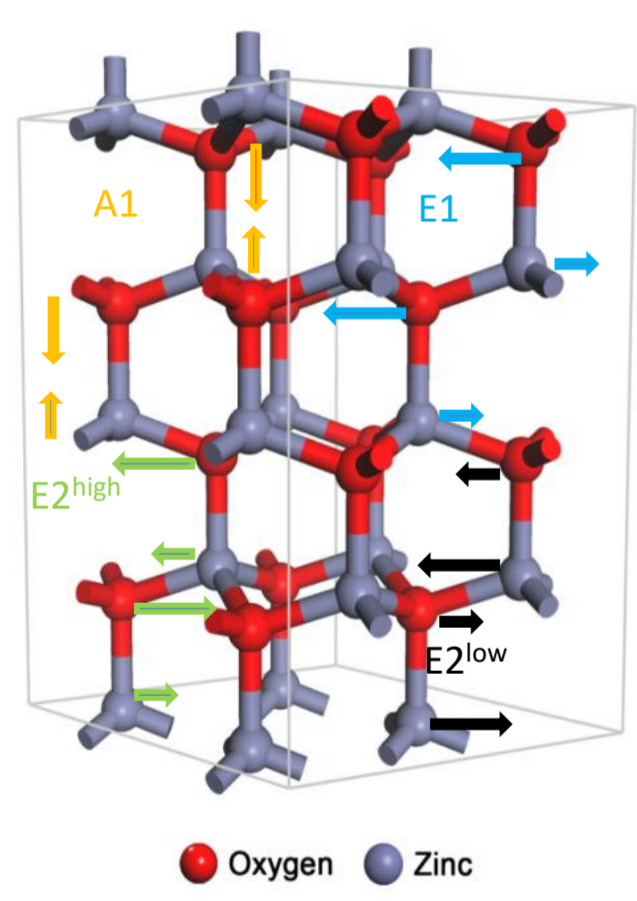
Defect levels in band gap of ZnO and related luminescence transitions:



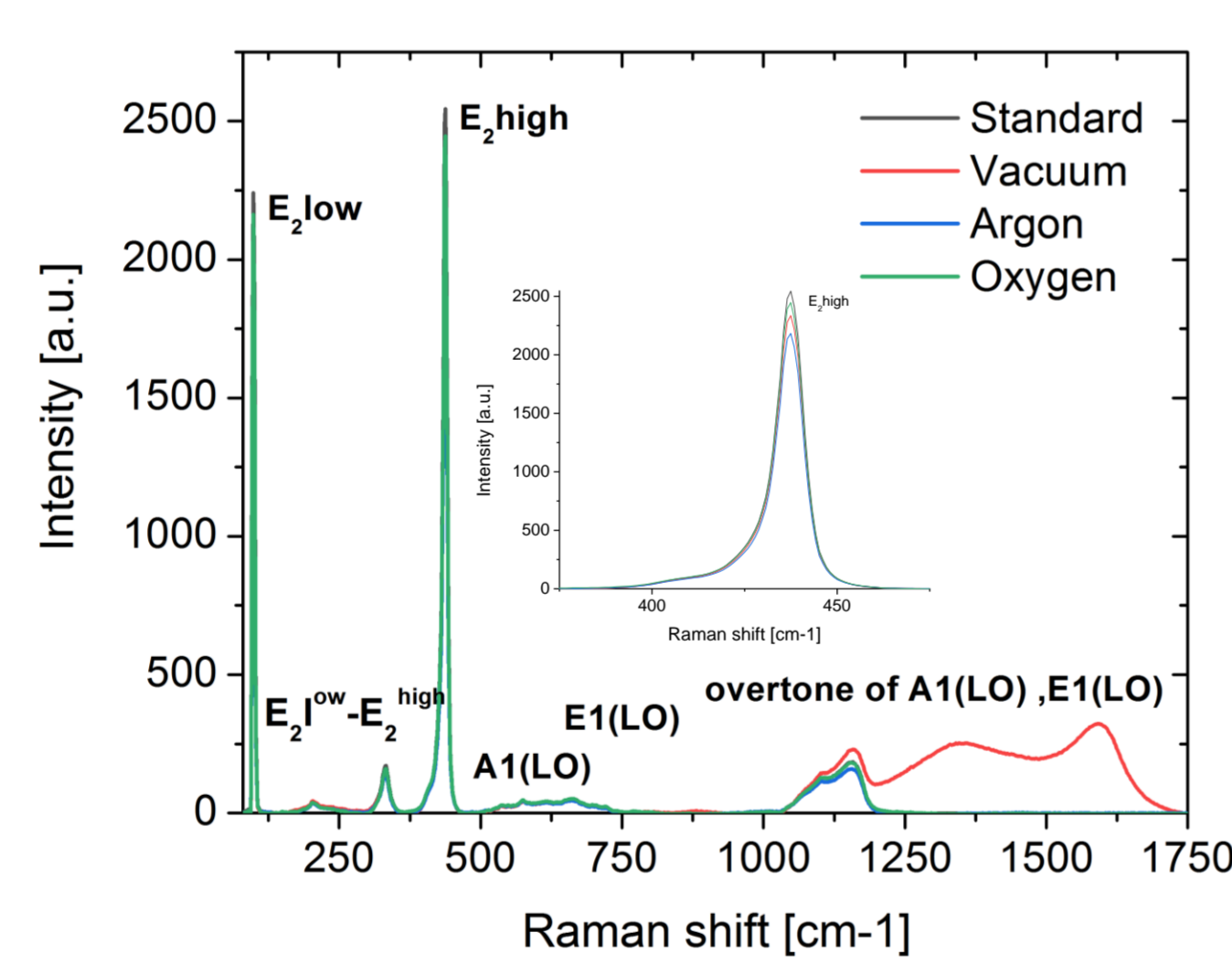
The luminescence spectra of ZnO measured at room temperature contain two characteristic bands - one sharp band in the UV region - NBE (near-band edge) - shows edge luminescence at 375 nm. Its origin is mostly excitonic - transitions of free excitons, bound excitons and also transitions between donor and acceptor pairs are used here. The origin of the second band in the VIS region – referred to as DLE (deep-level emission) – is currently being intensively studied and it is clear that it corresponds to intrinsic ZnO defects. DLE is a composite band that corresponds to the presence of various defects in the ZnO structure. Luminescence in the region 380-435 nm (purple) corresponds to the $Zn_i \rightarrow$ valence band (VB) transition; luminescence 435-500 nm (blue) corresponds to the transition between the conduction band (CB) $\rightarrow V_{Zn}$; luminescence 520-565 nm (green) corresponds to the transition between the conduction band (CB) and the oxygen vacancy (V_O) or the zinc vacancy V_{Zn} (or Zn_i); the luminescence between 590–625 nm (orange) corresponds to the transition between the conduction band (CB) and oxygen in the interstitial position O_i or between the oxygen and zinc interstitial positions $Zn_i \rightarrow O_i$; and finally, luminescence between 625–780 nm (red) is sometimes referred to as the transition between structural defects along the c-axis (such as Zn_i or V_O). A similar wide band was also measured on our standard samples.

RESULTS

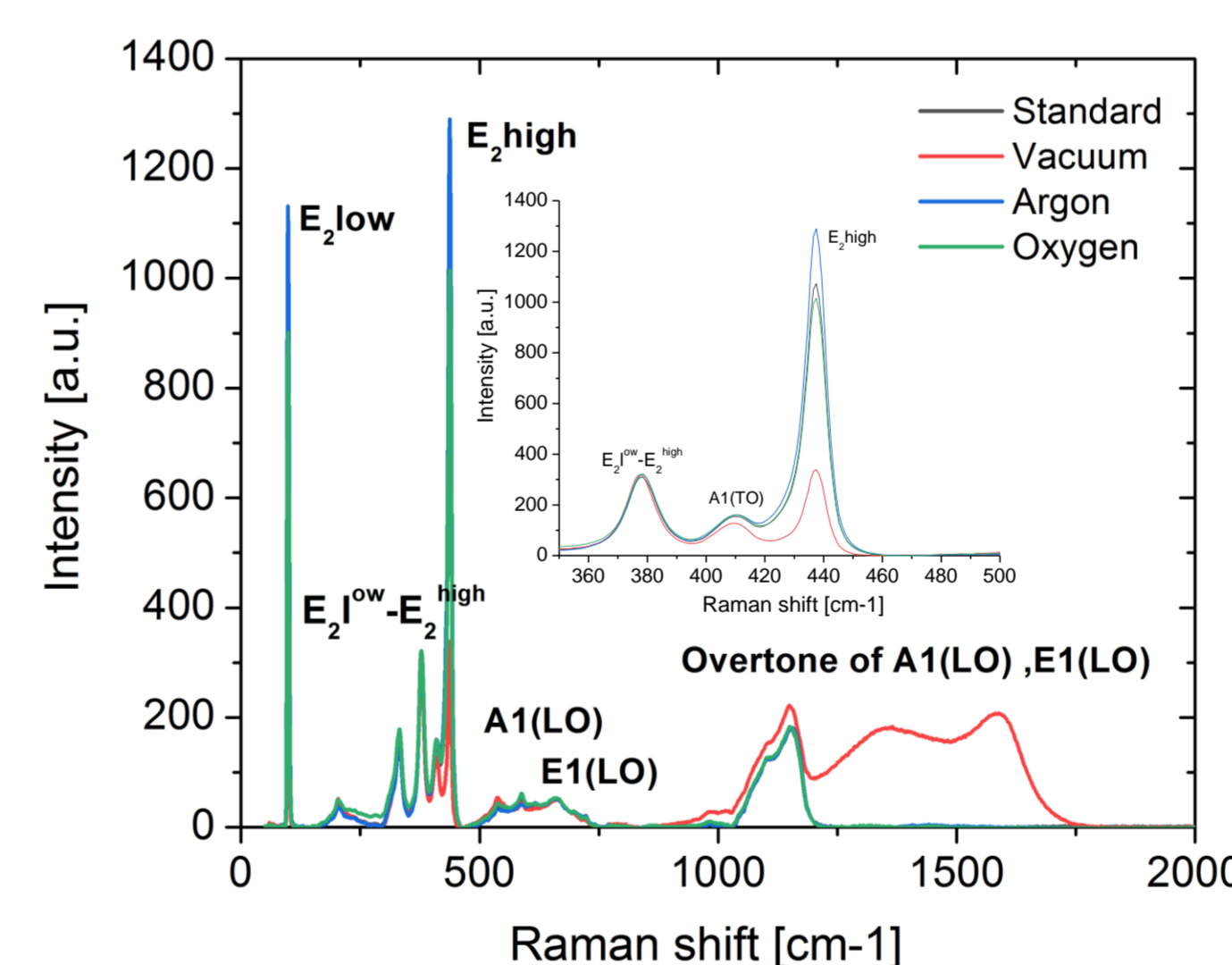
Raman spectroscopy:



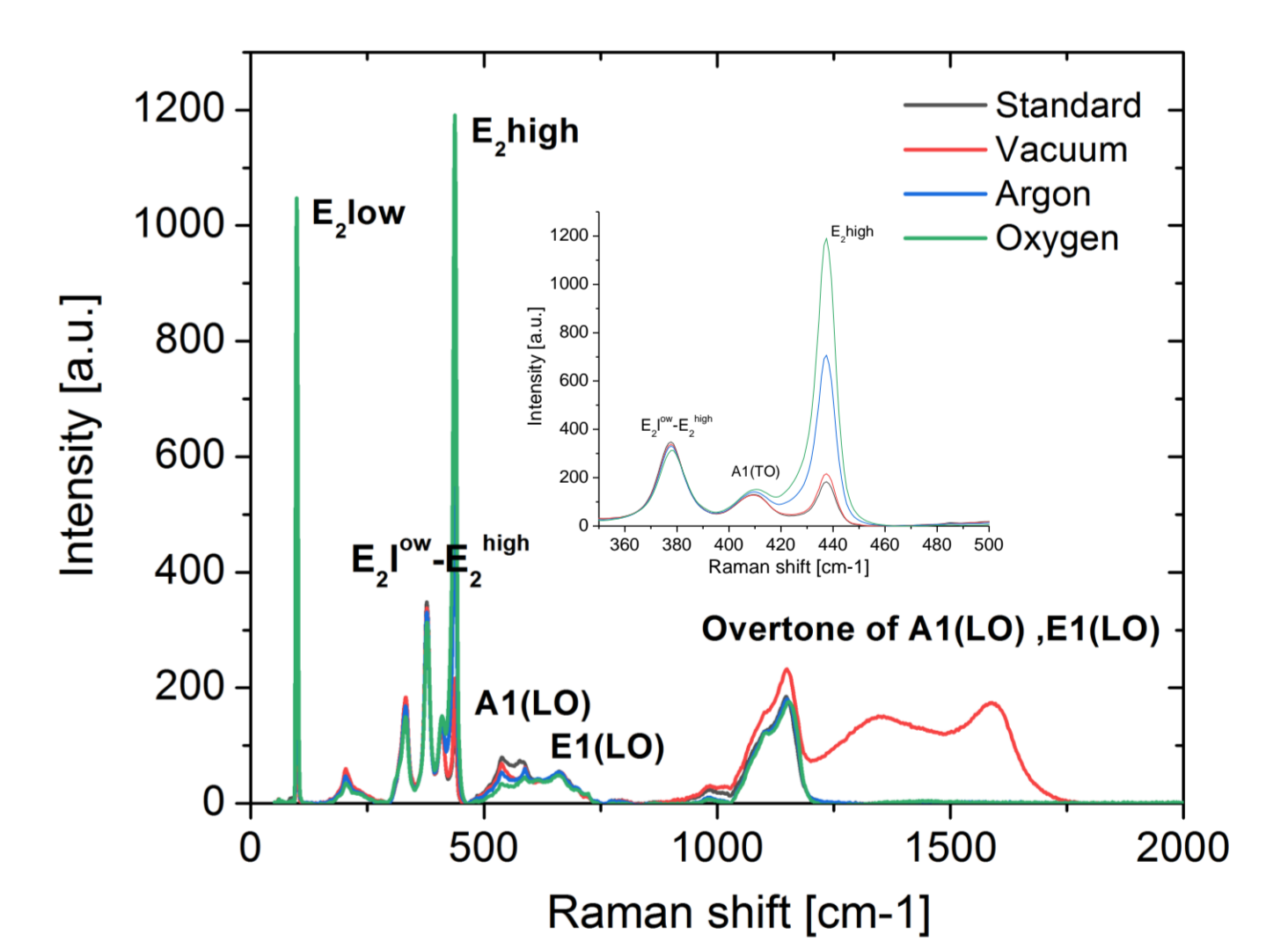
c-plane, Z-cut (0001)



a-plane, X-cut (11-20)



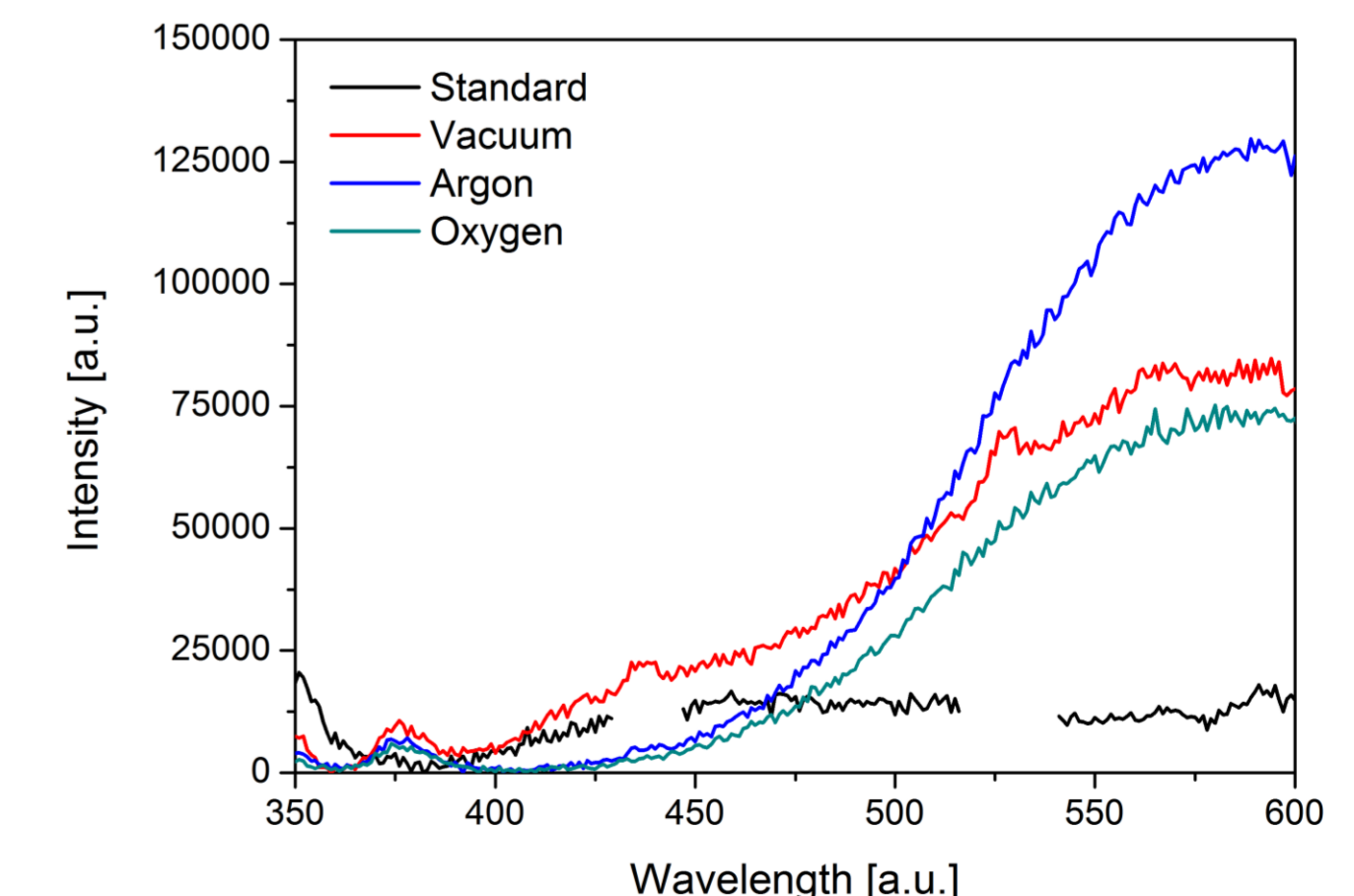
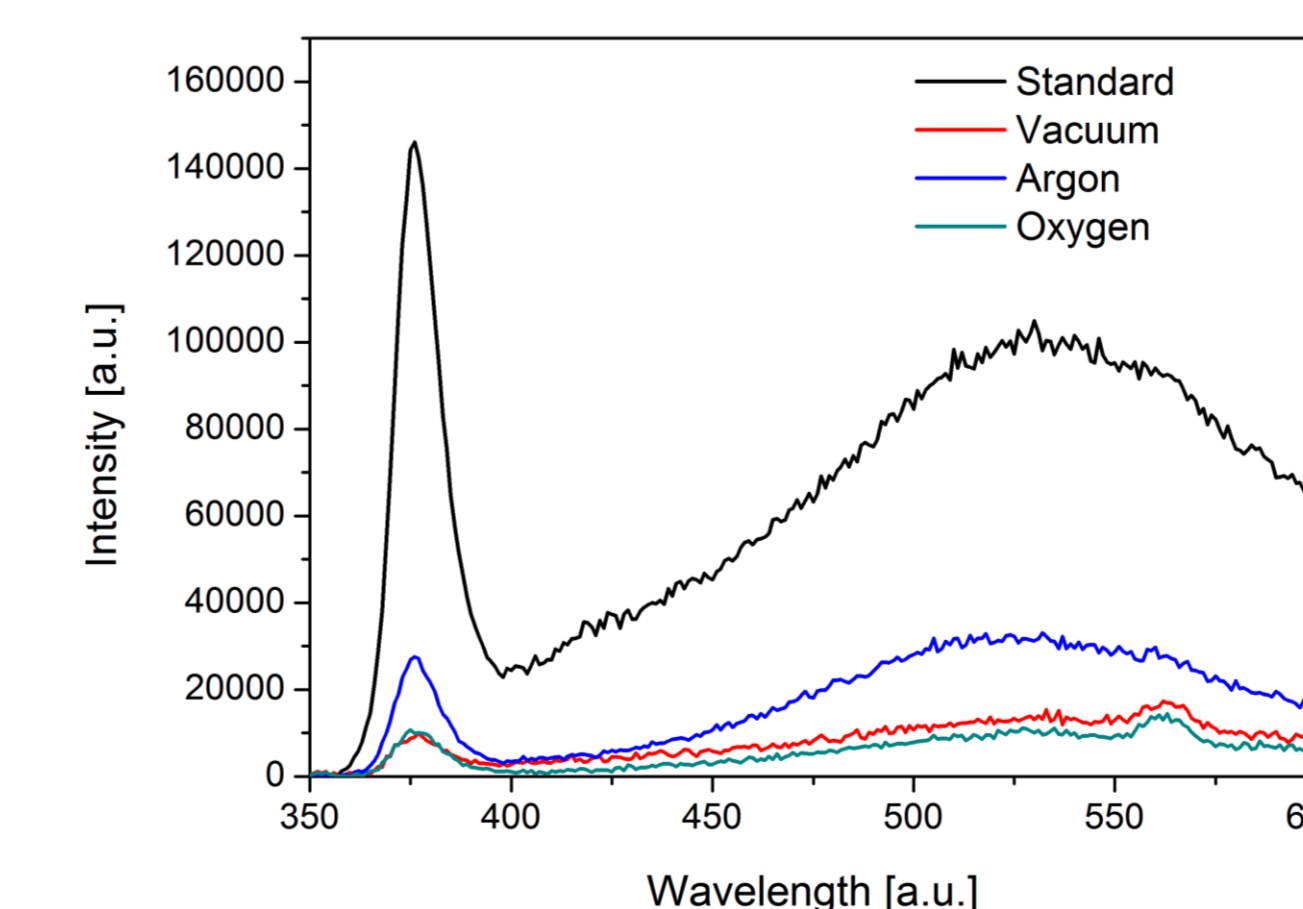
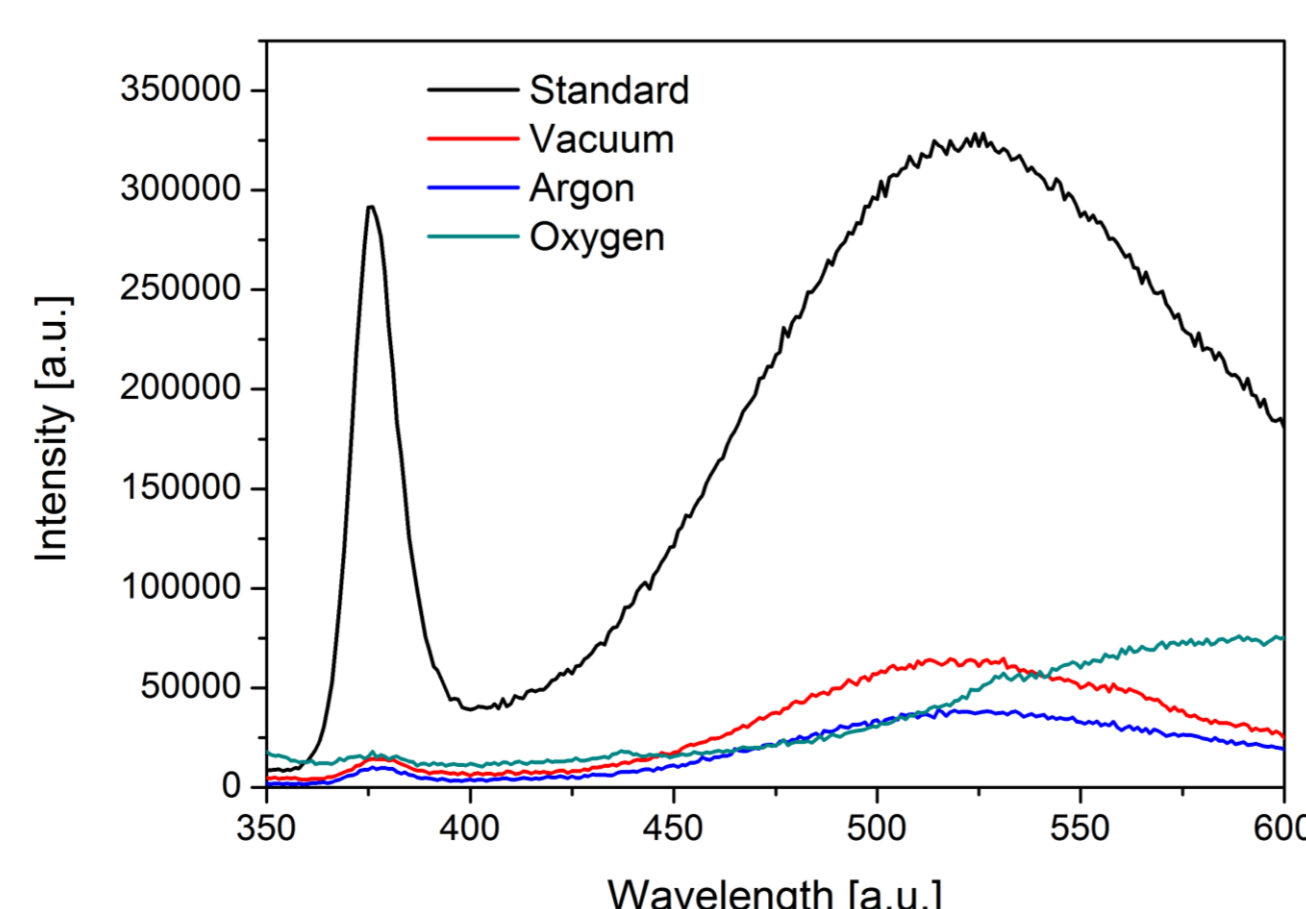
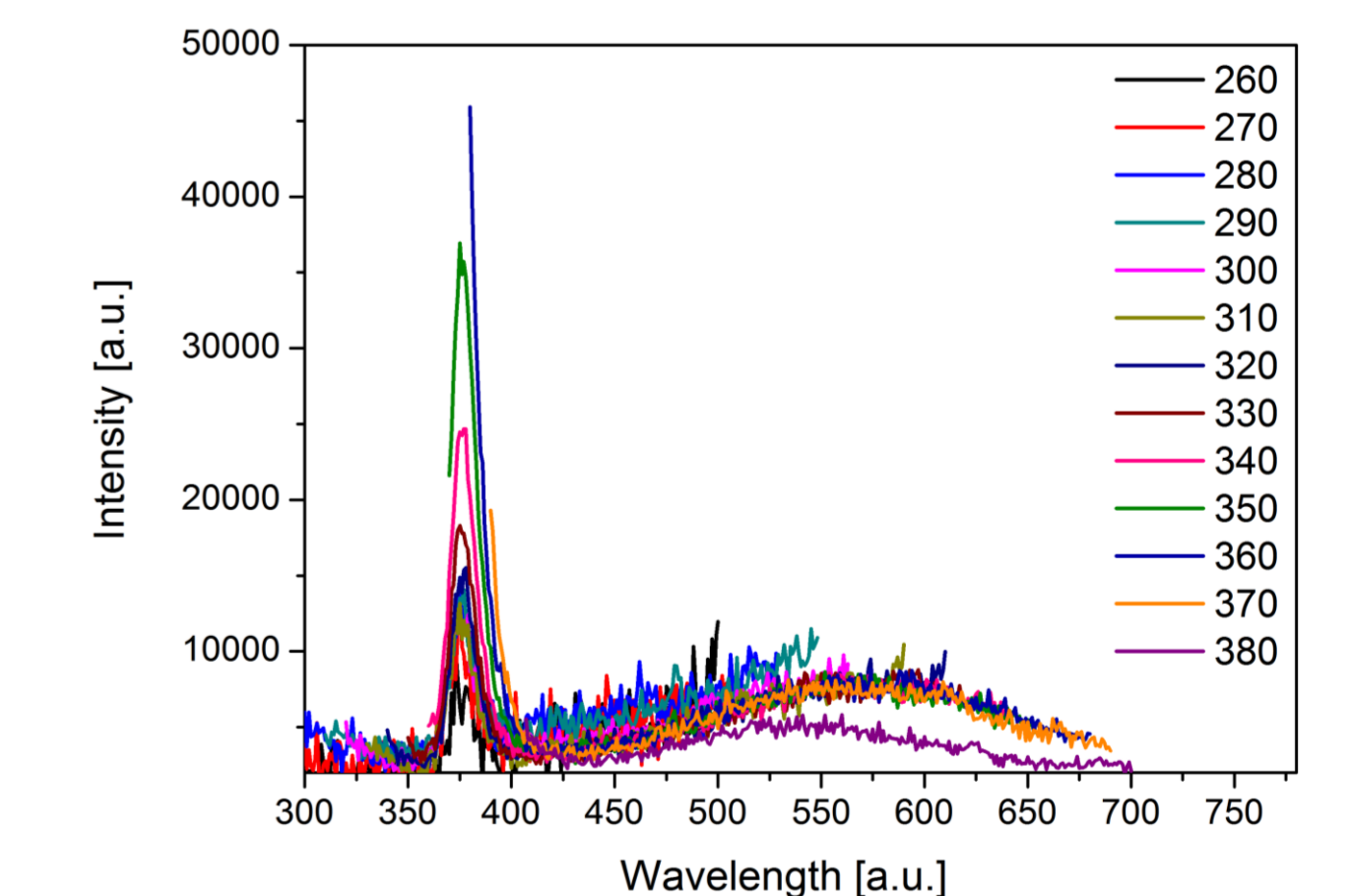
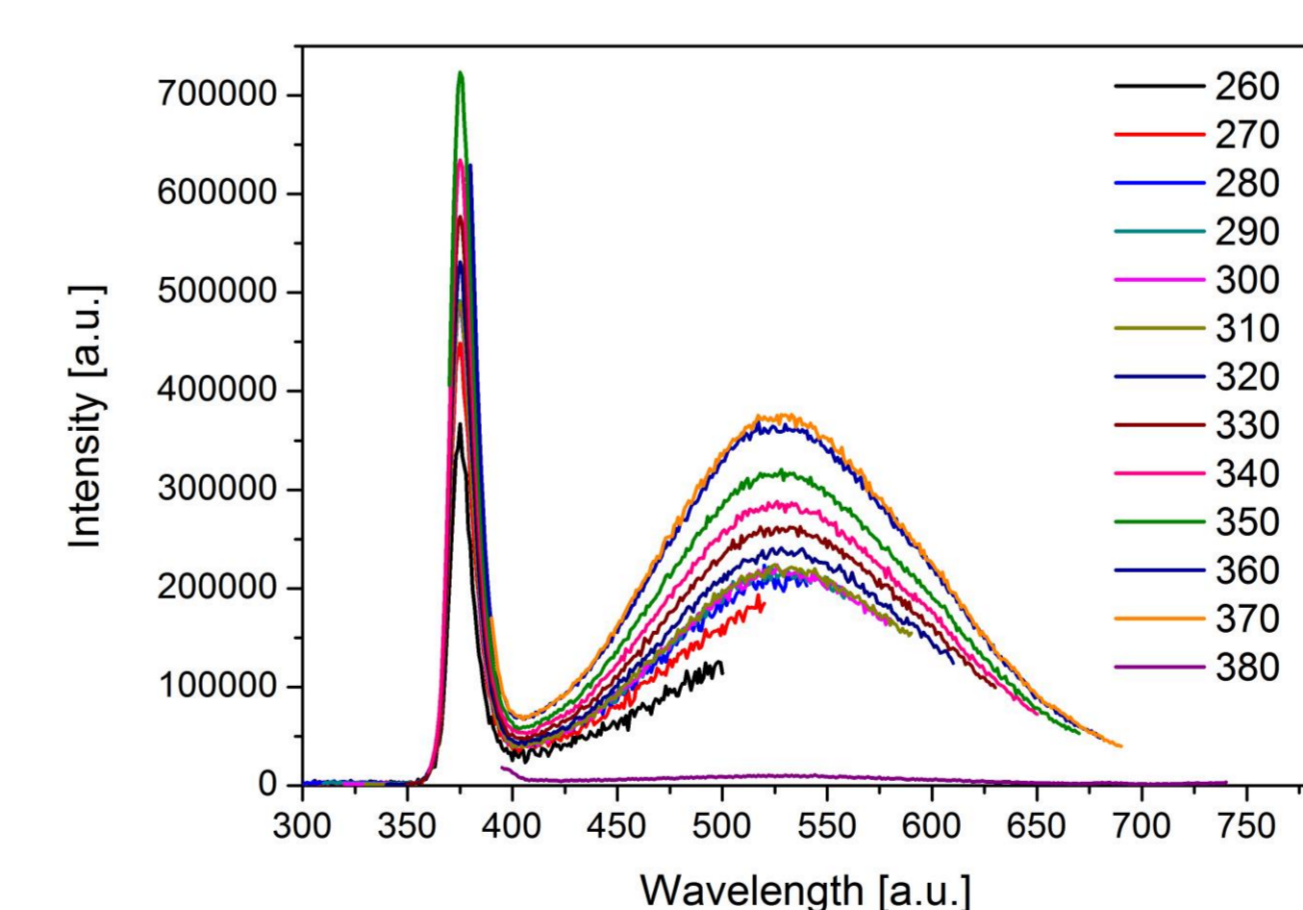
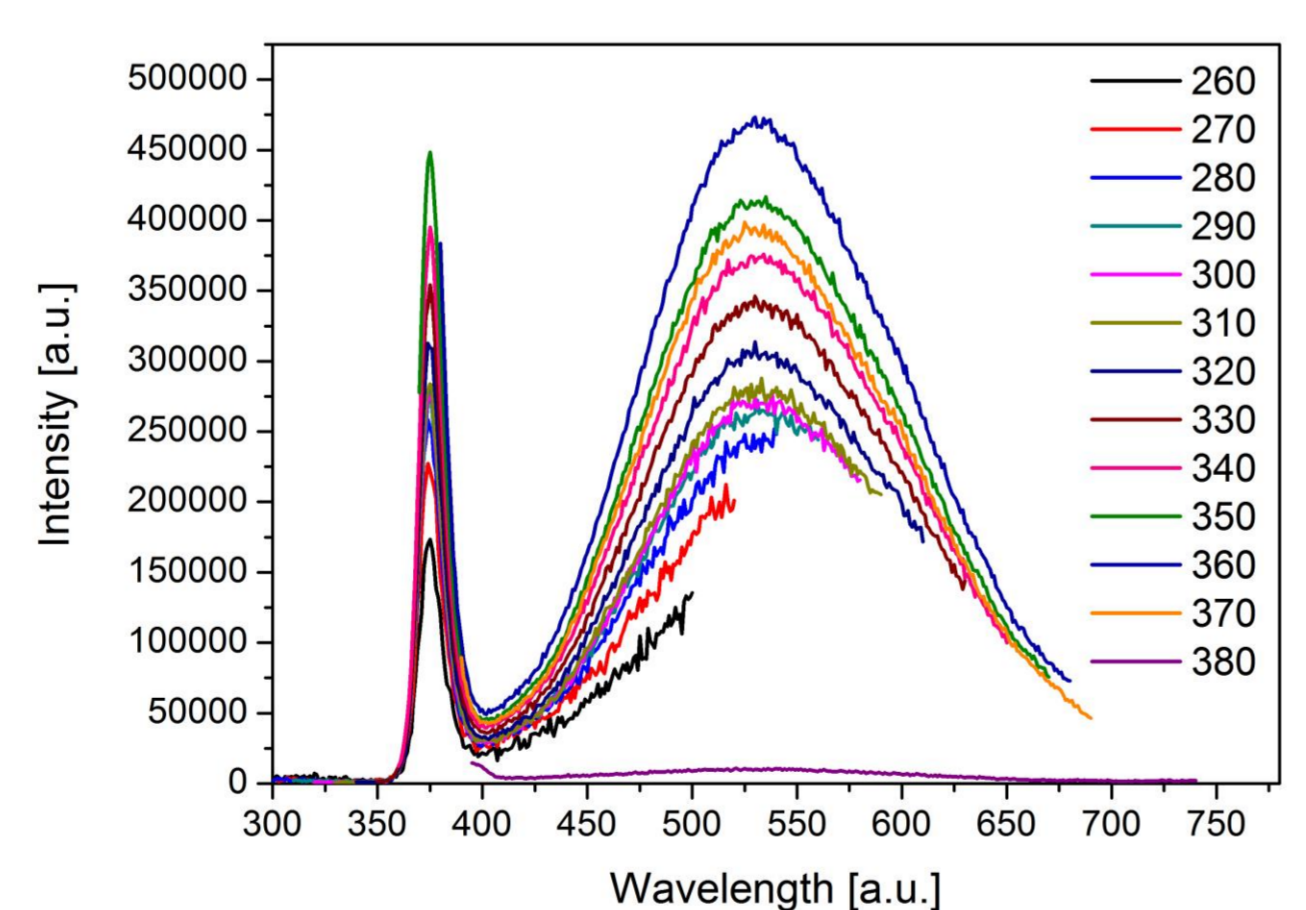
m-plane, Y-cut (10-10)



Luminescence:

Luminescence revealed substantial differences between crystallographic cuts:

- Highest luminescence was detected in c-plane, while very low luminescence in m-plane ZnO.
- Optimal excitation wavelengths were 280 nm for c-plane and 350 nm for a-plane.
- Annealing in different atmospheres caused lowering of NBE and DLE emission bands.
- Annealing also caused shift of the DLE band maximum to longer wavelengths – possible creation of V_O and O_i .



CONCLUSIONS

- The influence of different atmospheres during annealing on the movement of structural defects in the ZnO single crystal was confirmed
- The behavior of the used crystallographic cuts is different - the clear influence of the surface of single crystals on the movement of oxygen and its defects through the structure of ZnO was thus confirmed.
- In ZnO (10-10) cut annealing caused an increase in DLE luminescence, while in other crystallographic cuts the significant decrease of DLE luminescence was observed.

References:

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