

Positron-Annihilation, Structural and Optical Studies on Properties of Nanostructured ZrO_2 , ZnO , Bi_2O_3 and $\text{ZnO-Bi}_2\text{O}_3$

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Nanostructured oxides, like ZrO_2 , on ZnO and Bi_2O_3 show interesting electronic and photovoltaic properties. Pressed and annealed samples were obtained from nanopowders grown in hydrothermal or plasma processes. Positron annihilation (the Doppler broadening depth-resolved, positron lifetime) techniques were used to trace structural changes in samples after annealing. Photoluminescence spectra of all investigated samples show broad-band emission in the visible, with intensity depending on annealing temperature. The change in nanoporosity and positron lifetimes correlate well with changes in photoluminescence properties. The nature of broad photoluminescence bands is to be understood; further positron studies via the Doppler coincidence method would help in identifying the nature of defects in these samples.

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1. Introduction

Nanostructured oxides (ZnO , ZrO_2 , Bi_2O_3) find potentially numerous applications, from gas sensors, electronics, photoelectronic cells in near ultraviolet and high-temperature fuel cell membranes, see e.g. [1]. The main obstacle in their industrial use are difficulties in reproducible production with well defined properties [2]. For an example, bulk zirconia (ZrO_2) is usually stabilized by yttrium. The hydrothermal growth technique allows to obtain pure ZrO_2 with a controllable nanostructure [3]. Other techniques have been used to obtain nanostructured samples of ZnO and Bi_2O_3 . Samples were characterized by structural, optical and positron-annihilation techniques.

2. Sample preparation and characterisation

The ZnO , Bi_2O_3 nanopowders and the $\text{ZnO:58wt\%Bi}_2\text{O}_3$ nanocomposite have been prepared by evaporation of coarse grained commercially available oxide powders into a radio-frequency air plasma. The growth of particle and their size were controlled by

introducing cold gas into reaction chamber. Nanostructured samples were formed from nanopowders under pressure at 130 MPa and 50 MPa for ZrO_2 and Bi_2O_3 , respectively, and sintered at 700–800 °C and 450–550 °C in air for 30 min. Samples ZrO_2 underwent additional annealing at 700–900 °C in oxygen-containing atmosphere. Atomic force microscopy shows nanostructured morphology on the surface.

Chemical and phase compositions of powders produced were determined by conventional chemical and X-ray diffraction analysis (Advance, Bruker). The specific surface area was determined by argon adsorption-desorption method. The particle shape was examined by transmission electron microscopy (TEM). According to the TEM studies the ZnO powders are composed from whiskers-like particles, but particles of Bi_2O_3 and composites have spherical forms. The specific surface area of the powders was in the range of 23.2–24.1 m²/g.

All ceramic samples were characterized by means of highly resolved optical spectroscopy. Visible emission and excitation spectra were measured using the PTI QuantaMaster-based spectro-fluorimetric system, equipped with double monochromators in the excitation and emission paths and enabling cw and pulsed excitations over a wide spectral range (200–1000 nm) as well as signal detection within the spectral range from 220 nm

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to 10 μm . All optical measurements were taken at room temperature.

Positron annihilation spectroscopy (PAS) [4] is a powerful tool in analyzing defects in semiconductors, glasses, porous materials etc. Presented positron measurements have been performed with two techniques:

1) Doppler broadening PAS (DB-PAS) at the Trento laboratory, using an electrostatic slow positron beam tunable in the 0.05–25 keV energy range allowing to scan to a depth scale from 1 nm to about 1000 nm [5].

2) Positron annihilation lifetime Spectroscopy in Toruń

laboratory with 180 ps time resolution, performing measurements in the bulk material [6].

3. Results

The high resolution diffraction patterns of single oxides show well defined characteristic maxima of ZnO or Bi_2O_3 while the composite powder involves both phases, but with Bi_2O_3 peaks predominant (Fig. 1).

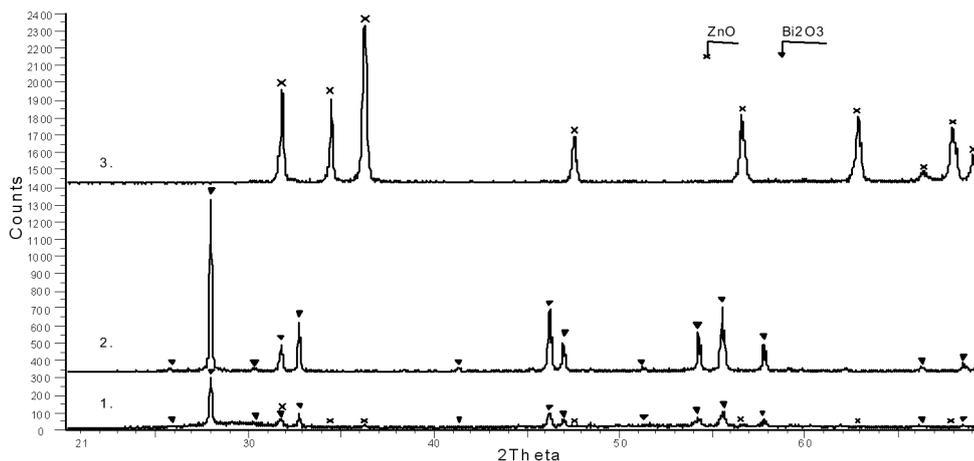


Fig. 1. High resolution diffraction spectra of the ZnO:58wt% Bi_2O_3 (1), Bi_2O_3 (2) and ZnO (3) samples.

The excitation spectra of ZnO samples annealed at temperatures 450–550 $^{\circ}\text{C}$ with emission monitored at 530 nm are shown in Fig. 2. For all samples a broad excitation band with maximum at 372 nm is observed, which can be attributed to the band gap absorption of ZnO (3.37 eV at room temperature [7]). The enhancement of photoluminescence is seen after annealing at 550 $^{\circ}\text{C}$.

Short wavelength emission spectra recorded under UV excitation are compared in Fig. 3. All spectra exhibit two distinct luminescence bands — narrow line located in UV region with maximum at 380 nm and broadband visible emission, extending from 450 nm to 750 nm.

The origin of the first band is related with so-called band-edge emission (recombination of free excitons between conductive band and valence band), reported e.g. in [8]. Second, much broader emission band extending from 450 to 750 nm results most probably from the presence of defects. The recently prevailing opinion is that the green luminescence in ZnO is originating from the photogenerated hole recombination with electron at the singly ionized oxygen vacancy [8]. Let us note that we observed a similar broad band under UV excitation also in ZrO_2 [3].

Figure 4 shows the luminescence spectra obtained under 370 nm excitation of ZnO:58wt% Bi_2O_3 samples differing in annealing temperatures. Also this material ex-

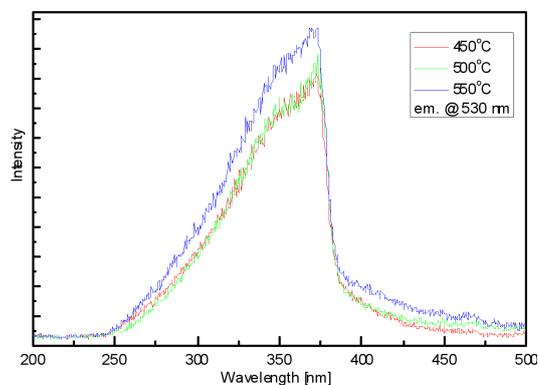


Fig. 2. Excitation spectra of ZnO samples for different annealing temperatures (emission monitored at 530 nm). A rise of the signal is visible after annealing at 550 $^{\circ}\text{C}$.

hibits a broad emission band, similar to those in ZrO_2 and ZnO. The intensity of the emission rises by a factor of three after annealing at 500–550 $^{\circ}\text{C}$.

Positron annihilation studies show in all samples several components of the lifetime, out of which the short one (i.e. 180 ps in ZrO_2 , 160 ps in ZnO) can be attributed to annihilation in a crystalline matrix. In all samples

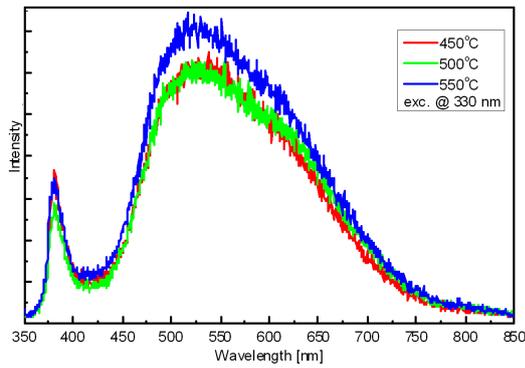


Fig. 3. Emission spectra of ZnO samples differing in annealing temperature.

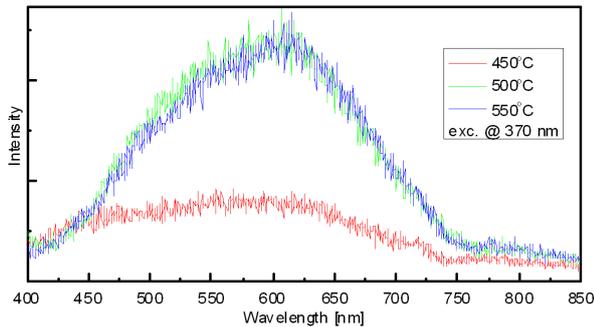


Fig. 4. PL emission spectra under 370 nm excitation for ZnO:58wt%Bi₂O₃ samples, differing in annealing temperature.

also a second component, of about 350–380 ps is present. In ZrO₂ we observe a sharply rising contribution of this intermediate lifetime, from merely 20% for samples annealed at 700 °C to 75% for samples annealed at 800 °C and decreasing slightly (to 70%) — for samples annealed at 900 °C. These changes correlate with the fall in PL intensity, which shows a similar abrupt variation between

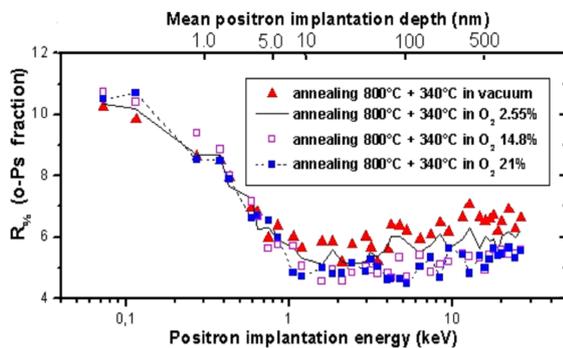


Fig. 5. The fraction of *ortho*-positronium annihilation in nanostructured pure zirconia samples, treated at 800 °C and further annealed in oxygen–nitrogen atmosphere for 20 min with different O₂ contents.

700 °C and 800 °C. For ZnO the intermediate lifetime changes from about 380 ps to 420 ps and the intensity from 84% to 73% passing from the 450–500 °C to 550 °C annealing temperature. The change in lifetime value indicates a new type of trapping centers for positrons and correlates with the rise in the PL intensity. No such a clear effect is seen in ZnO:Bi₂O₃; further positron lifetime measurements are needed.

To determine the depth profile of free nanovolumes (in ZrO₂), the signal of 3- γ (*ortho*-positronium) annihilation was studied in DB-PAS experiment, see Fig. 5. The *o*-Ps signal falls from 10–11% in near-to-surface layers to 5–7% at 10–100 nm depth. Annealing in oxygen-rich atmosphere seems to seal the free nanovolumes, see Fig. 5. The porosity lowers after annealing at 800 °C as compared to samples annealed at 700 °C.

The observed correlations in change of positron-annihilation lifetimes and DB-PAS spectra with the changes in PL intensities indicate the defect nature of the broad emission peaks. Presence of defects is to be expected also from high resolution TEM spectra of our pilot samples. In order to determine if these defects and/or structural changes are related to oxygen atoms and/or oxygen clusters, an additional positron technique (i.e. the Doppler coincidence) [5] have to be applied.

Acknowledgments

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