EFFECT OF NANOPOWDERS MORPHOLOGY ON THE ZnO CERAMICS STRUCTURE AND PROPERTIES

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Introduction. Investigation of ZnO crystals is of special interest because of their potential for applications in optoelectronics, sensors, spintronic etc. Recently, the attention of research community has increasingly turned to ZnO ceramics from nanopowders [1,2]. The authors in [2], obtained for the first time transparent ZnO ceramics, have shown that these ceramics are of interest for use as high-efficiency fast scintillators. This requires high intensity of X-ray or photoluminescence (PL) exciton peak, negligible defect-associated ("green") PL, subnanosecond decay time and high hardness without grain-boundary (GB) brittleness. These requirements should correlate with the high quality microstructure. However, sintering of ZnO ceramics largely is determined by the powder interactions at the initial state, tendency of nanopowders to faceting and to quick agglomeration. The fast agglomeration is due to high surface (*S*)-to-volume (*V*) ratio (*S/V).* However, it is known that ZnO has the variety of 2D and 3D ZnO nanocrystals forms such as nanowires, nanocombs, tetrapods etc . Such nanostructures as tetrapods have large free surfaces with minimal energy in the direction of growth and low (*S/V).*parameter. For these shaped particles other sintering processes may take place in all sintering stages. On the other side, the problems of ZnO powders agglomeration can be solved using hot pressing and by impurities doping.

In this work the role of the ZnO nanopowders morphology in structural, mechanical and optical properties of ZnO ceramics obtained by high temperature (1200^{0}C) sintering (HTS) and by uniaxial hot pressing (UHP, 1150^{0}C) was investigated.

Experimental ZnO nanopowders for HTS were obtained by a method of Zn evaporation, oxidation and condensation in a tube furnace at 950^{o}C [3]. By varying conditions of oxygen flow and temperature gradient we obtained tetrapods (*d*=50-100 nm, *l*=3-10 μm) (Fig1,a,b) and grained (*d*=100-200 nm) faceted powders (Fig1,c).

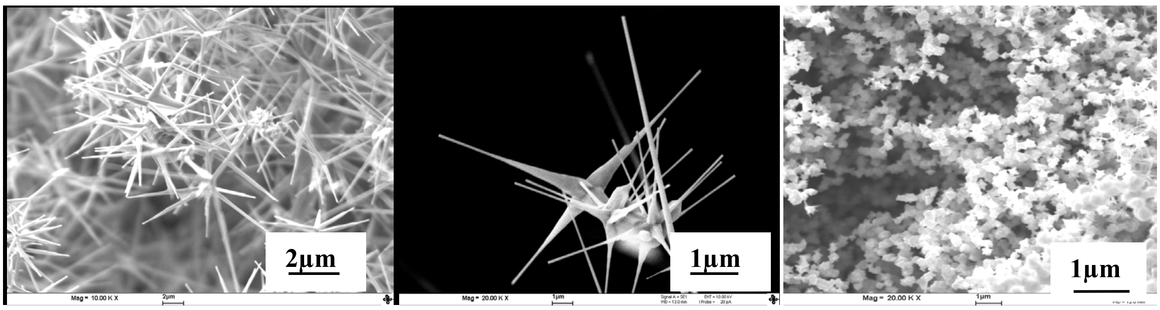

Figure 1 - SEM images of ZnO powders morphology: tetrapods-like (a,b) and grained powders (c)

For UHP sintering nanopowders were obtained by chemical methods, indium as dopant (0.13wt%) was introduced in the form of indium oxide by mechanical mixing with ZnO [2]. Powders and ceramics structural state have been investigated using SEM, TEM, XRD, EDS and photoluminescence (PL) methods. Mechanical properties (hardness H,GPa, elastic modulus E,GPa and plasticity) of ceramics were characterized by the nanoindentation.

Rezults and discussion. As can be seen from Fig.1, structural elements of tetrapods (long rods) remain straight during process of obtaining (a,b). In contrast with tetrapods grained powders, are faceted and strongly agglomerated (c). Comparative analysis of HTS ceramics microstructures showed that all ceramics have recrystallized grains. However, ceramics obtained from grained powders had quite large, inhomogeneous grains (d=6-10 μm) and high (10-8%) porosity both at the grain boundaries (GBs) and inside grains. Fracture is characterized as brittle intragranular and intergranular that reflects the positions of previous low-angle GBs in conglomerate as locations of micropores [3]. Ceramics from tetrapods had fine-grained structure (d=1-4μm) without signs of grain boundary brittleness. During sintering tetrapod-like particles transformed into grains with randomly misorientated large-angle GBs which are efficient paths for atomic transport and densification. Such GBs are instrumental in eliminating residual porosity and point defect. Values of hardness (3.8GPa), modulus (E=120GPa) and data for PL spectra are comparable to properties of fine-grained ZnO films. The calculated value of PL parameter $\alpha = I_{def}/I_{exc}$ is very small α = 0.025 and thus it indicates a high quality of this ceramics. However, HTS ceramics even based on tetrapods are not transparent, but allow in perspective use as gas sensors.

Investigated hot pressing ceramics (UHP) based on grained powders were optically transparent due active plastic deformation at high temperature leading to the close and dissolution of initial micropores, but have GBs brittleness. Moreover, decreased values of elastic modulus within a grains and a wide defect-associated ("green") PL band at 2.2-2.8 eV in conjunction with a weak excitonic band (Fig.2) indicate on a high concentration of residual point defects. Stability of these defects is attributed to slow volume and low-angle GBs diffusion as well as to large distance to probable sinks at coarse grains (d=10-20 μm).

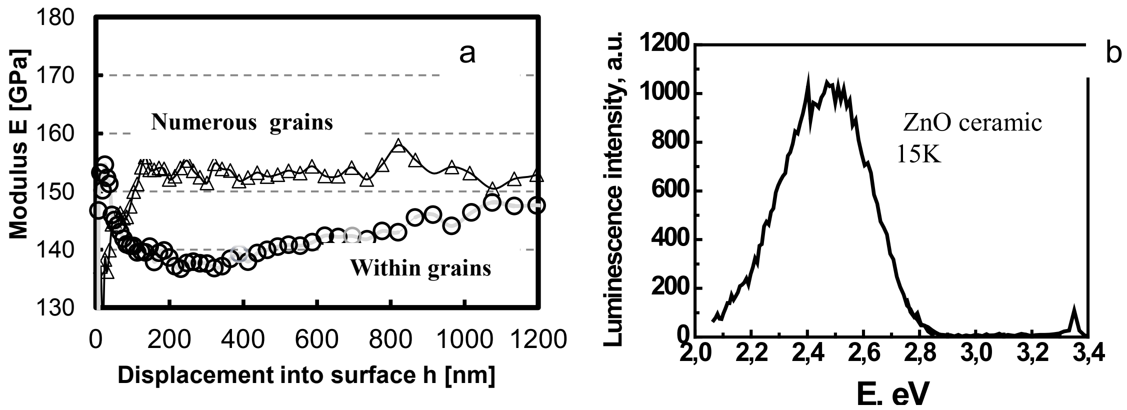

Figure 2 - Modulus *vs* displacement in to surface (a) and PL intensity (b) for hot pressing ZnO ceramics.

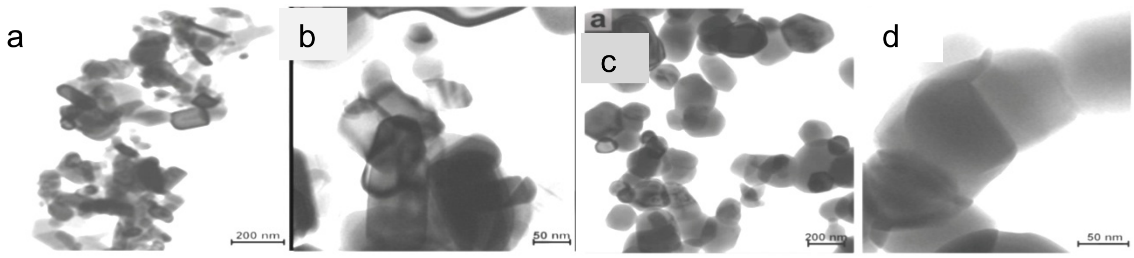

Figure 3 - TEM images of initial ZnO (a,b) and doped ZnO :In (c,d) powders.

It was found, that indium doping (0.13%wt) changes all properties of ZnO ceramics. Already during the mixing of powders indium induces a transition of initially faceted ZnO particles to rounded (Fig.3) that facilities the formation of diffusion mobility high-angle GBs. It was shown [2] that the introduction of the optimal concentration (0.13 wt.%) of indium leads to the increase of the intensity of *X-ray luminescence* excitonic band and ensures photonic response with a subnanosecond decay time. Indeed, our data of PL confirm this as is seen from Fig.4,a. In ZnO:In ceramics the main excitonic band at 15K is at 3.35 eV and its origin is exciton bound at neutral donor (ExD^0), whereas the (defect associated) "green" luminescence is negligible. The calculated values of PL parameter $\alpha= I_{def}/I_{exc}$ at 293K for undoped ZnO ceramics was α= 1.2, for indium doped α= 0.08 is decreased in 15 time compared with undoped. Thus, the indium doping facilities the elimination of points defects.

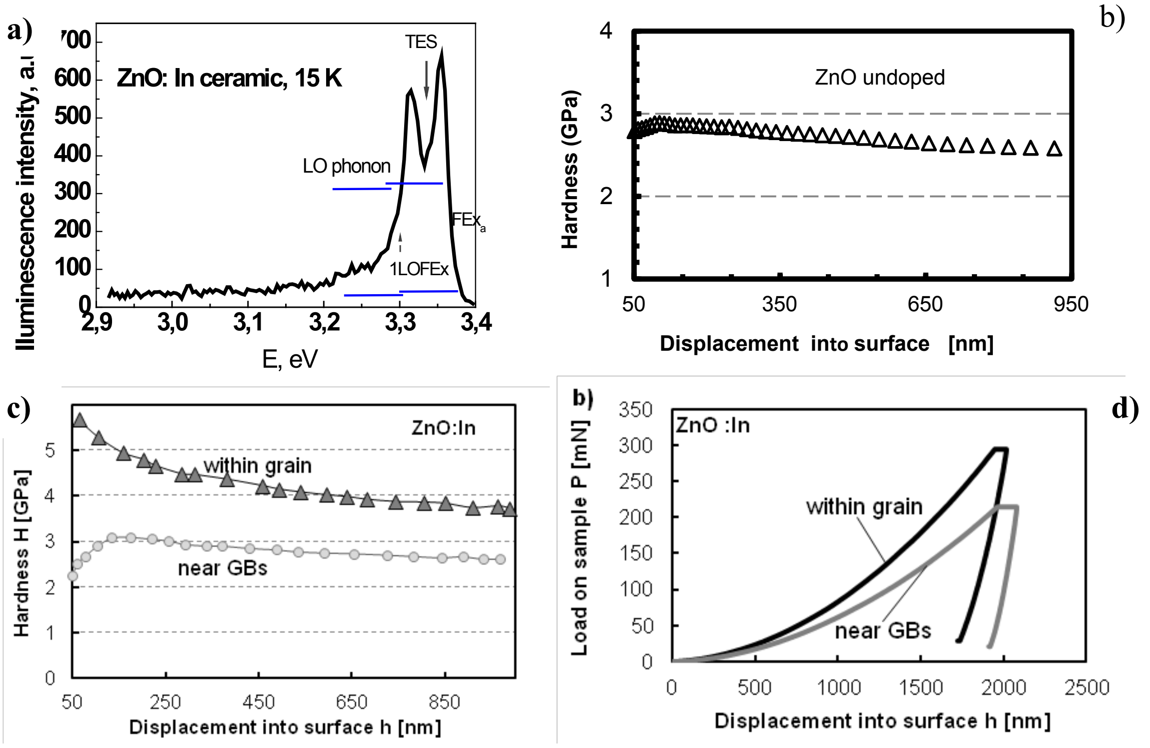

Figure 4 - The photoluminescence spectra measured with time gate 125ns at T= 15K (a), and nanoindentation data (b),(c) ,(d) for ZnO:In ceramics.

The hardness results are presented in Fig.4.,b,c,d. The nanoindentaion was carried out both at the center of the coarse grains and near the GBs using the technique of topographic indentation"*in situ*" in nanoindenter tester. In comparison to the undoped ZnO ceramics the hardness in the volume of doped ceramics is 1.4 times higher. At the same time the plasticity of GBs layers has been revealed from analysis of loading curves (Fig.4,d). Calculation of the work of plastic deformation shows greater plasticity for the "GBs group" in comparison to the "within grain" (90.5 % *vs* 81 % which consequently) that determined the absence of grain-boundary brittleness in ZnO:In ceramics.

Conclusion The results affirm the major influence of powders morphology on the structure, mechanical and optical properties of ZnO ceramics. A comparative analysis showed that doping with indium lead to the faceting-rounding transition of initially ZnO particles which promotes the formation of diffusion-active high-angle (GBs) and good properties of ceramics. Results characterize ZnO:In ceramics as a prospective material for fast scintillators.

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References

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