

EFFECT OF IN DOPING ON THE ZnO POWDERS  
 MORPHOLOGY AND MICROSTRUCTURE EVOLUTION  
 OF ZnO:In CERAMICS AS A MATERIAL FOR  
 SCINTILLATORS

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Transparent ZnO ceramics are of interest for use as material for high-efficiency fast scintillators. Doping ZnO ceramics in order to improve complex of their properties is a promising direction. In the present research, the role of indium in the ZnO nanopowders surface interactions and in the change of microstructures and photoluminescence (PL) characteristics of sintered ceramics is considered. Undoped and 0.13 wt% In doped ZnO ceramics are obtained by hot pressing sintering. It has been found that indium leads to the transition of initially faceted ZnO particles to rounded, contributing to good sintering with formation of diffusion active grain boundaries (GBs). Unlike ZnO ceramics, ZnO:In ceramics microstructure is characterised by the transcrystalline mode of fracture, faceted GBs with places of zig-zag forms and predominant distribution of In at the GBs. Such indium induced modifications of GBs promote removal of point defects and reduce PL parameter  $\alpha = I_{\text{def}}/I_{\text{exc}}$  in comparison with the undoped ceramics. Results characterise ZnO:In ceramics with improved GBs properties as a prospective material for scintillators.

**Keywords:** grain boundaries, hot pressing sintering, In doped ZnO ceramics, photoluminescence, ZnO powders

## 1. INTRODUCTION

ZnO as a multifunctional material continues to be the subject of thorough study for many years. The interest in ZnO remains high due to potential applications of various ZnO nanostructures [1], [2] and due to new opportunities for nanocrystalline films, coatings and ceramics obtained by more efficient technologies [3]–[5]. Possibilities of using ZnO as a polycrystalline material have stimulated theoretical and experimental research in the field of surface energy, features in surface states and grain boundaries (GBs) in ZnO systems [6], [7].

These findings are important not only for conductive transparent ZnO thin films but to an even greater extent for sintered ZnO ceramics based on nanopowders. Transparent ZnO ceramics are of interest for use as high-efficiency fast scintillator. This requires high intensity of radioluminescence or photoluminescence (PL) exciton peak (3.36 eV), negligible point defect associated “green” peak (2.45 eV), subnanosecond decay time and absence of GBs brittleness [8], [9]. To ensure such properties, a high-quality microstructure without micropores and with the minimal number of point defects should be formed during the sintering of ceramics. As known, the sintering process is determined not only by technological parameters but also by the powder interaction in the initial state and the behaviour of GBs at the stage of grain growth [10]. Sintering of ZnO ceramics presents certain difficulties due to the variety of ZnO nanopowder morphological forms and their tendency to quickly agglomerate, which can lead to the residual pores, high concentration of point defects and GBs brittleness [11], [12]. The method of hot pressing ZnO powder activates volume diffusion, which helps eliminate the porosity of the ceramics; however, as we have shown earlier, it is practically difficult to eliminate the presence of point defects even during hot pressing [12]. On the other hand, it is known that introduction of donor impurities such as gallium or indium into the composition can alter the properties of ZnO nanocrystals and films [3], [13]. In [14] for the first time ZnO:In transparent ceramic has been obtained by hot pressing sintering in vacuum. It has been shown that the indium doping leads to the increase of the intensity of X-ray luminescence excitonic band and ensures photonic response with a subnanosecond decay time. To understand the nature of In effect on ZnO:In ceramics properties, in the present research we consider the influence of indium on the powder interaction and microstructure formation during sintering.

## 2. EXPERIMENTAL PART

Commercial zinc oxide powder (99.9995 %, “Alfa AESAR”, USA) was used to obtain ceramics. The indium in the form of indium oxide (UHP, Russia) was introduced by mechanical mixing with the original ZnO powder during 40 min at 293K. Ceramics of undoped and 0.13 wt% In doped ZnO were fabricated by uniaxial hot pressing sintering in vacuum at temperature 1150 °C and  $P = 100\text{--}200$  MPa for 60 min [14]. Microstructures were investigated by scanning electron microscopy (SEM, LYRA, Tescan, Oxford, HV:15-40 kV) with energy dispersive X-ray spectroscopy (EDS, Eagle III XPL), transmission electron microscopy (TEM, FEI, Tecnai, GF20) and optical microscopy (Eclipse L150, Nikon). Photoluminescence (PL) was mea-

sured under YAG: Nd laser excitation (266 nm, 2 ns pulse) at 293 K. The ratio value of “defect” to excitonic PL intensities ( $\alpha = I_{\text{def}}/I_{\text{exc}}$ ) was measured by using 125 ns time gate. The luminescence was recorded with a phonon counting head (HAMAMATSU H8259) and photon counting board Fast Com Tech module P 7887 with 500 channels and minimal time bins of 250 ps. The monochromator MDP-3 was used for spectral measurements.

### 3. RESULTS AND DISCUSSION

#### 3.1. Powder Morphology

Figures 1, a,b,c are TEM and SEM images showing the morphology of undoped ZnO powders. The original ZnO powder (Fig. 1,a,b,c) is characterised by a considerable inhomogeneity; it contains faceted particles: nanograins ( $d_g = 25\text{--}50$  nm), nanorods ( $d_g = 20$  nm,  $l = 100$  nm) and thin elongated nanobelts ( $l = 100\text{--}200$  nm). Strong agglomeration of these powder particles is observed – in the form of chains, rings and relative large platforms. The aggregation of individual nanorods occurs by orienting the outer facets, mostly prismatic (1010) non-polar low energy planes (shown in Fig. 1,b with arrows).

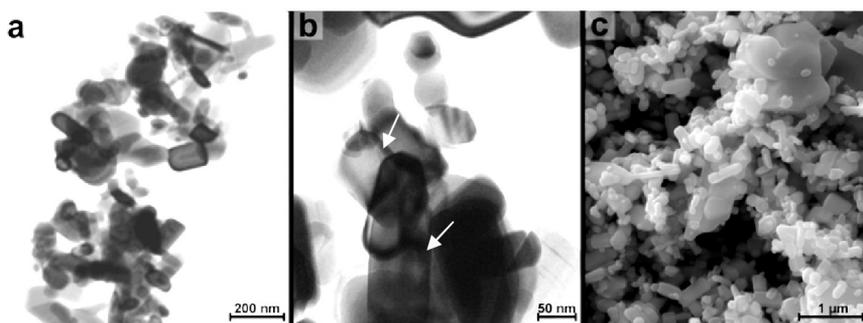


Fig. 1. TEM (a, b) and SEM (c) images of initial (original) ZnO powder.

Addition of indium leads to a significant change in the original ZnO powder morphology. As can be seen from Fig. 2 a,b,c, the general trend under the influence of indium is the rounding of original ZnO faceted particles. Large ring-shaped aggregates or large platforms in this case are almost absent.

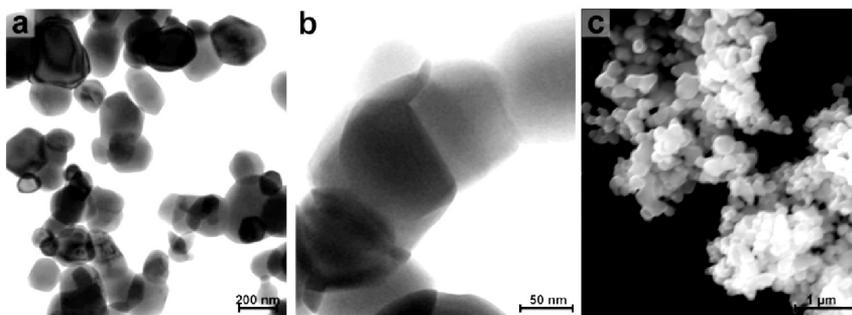


Fig. 2. TEM (a, b) and SEM (c) images of ZnO:In 0.13wt% powders.

An unique non-faceted ZnO:In aggregates are formed, in which roughed GBs and triple junctions are visible. Thus, it has been found that already during the mixing of powders indium facilitates a transition of initial faceted ZnO particles to rounding. As it is known, rounded particles are preferable for sintering due to spontaneous adhesion determined by the surface self-diffusion and formation of diffusion active high angle GBs on the contact [4], [10], [17].

It should be noted that the ability of indium to change the shape of ZnO nanoparticles during contacting has not been investigated. However, the reaction between ZnO and  $\text{In}_2\text{O}_3$  at 1100 °C has been studied in [18], where phase diagram of ZnO- $\text{In}_2\text{O}_3$  is presented. Thus, it is known that ZnO can interact with In *via* solid state reactions forming compounds  $\text{ZnO}+\text{Zn}_7\text{In}_2\text{O}_{10}$ . In our case, these interactions occur on the contact surfaces, so it is necessary to take into account the thermodynamic features of the ZnO surface planes. In many theoretical studies [6], [7], [19] the calculations reveal that the surface energy  $\gamma$  of Zn-0001 polar plane is higher ( $\gamma_{\text{zn}} = 2.0 \text{ J/m}^2$ ) than that of O-0001 ( $\gamma_{\text{o}} = 1.6 \text{ J/m}^2$ ). Zn-0001 surface is more unstable and active for interaction with such additive elements as Ga and In. From this point, the interactions of  $\text{In}_2\text{O}_3$  –ZnO occur via mechanical alloying [20] on the edges of Zn-0001 polar plane contacting with the non-polar plane. As a result, there is a violation of the atomic arrangement that leads to the faceting-rounding transitions [17] of powder surfaces and formation of stable ZnInO compound in local contact places.

### 3.2. Microstructure of Ceramics

In Fig. 3, a,b,c the microstructure of undoped ZnO ceramics is presented. The micrograph of undoped ceramics shows recrystallized isometric grains with sizes  $d_g = 7\text{--}25 \mu\text{m}$  (Fig. 3,a). Consideration of fracture characteristics, as the most informative and important for sintered ceramics, has shown that fracture of undoped ZnO ceramics (Fig. 3,b,c) has mainly brittle intergranular mode. Here, in some places, the presence of fractured substructure and elongated grains are visible. Fracture of them occurs by cleavage (Fig. 3,c). The heterogeneity of the initial powder structure is manifested in this ceramics.

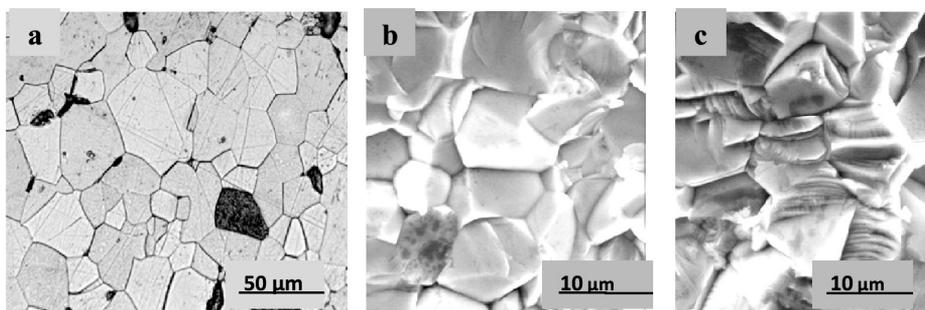


Fig. 3. Micrographs of etched external surface (a), and SEM images of fracture surfaces (b),(c) of sintered undoped ZnO ceramics.

Completely different unusual microstructures have surfaces in In doped ceramics (Fig. 4, a,b,c). In general, the microstructure is smaller ( $d_g = 2\text{--}5 \mu\text{m}$ ) than for undoped ceramics. Furthermore, in the structure there are faceted GBs, some grains

are elongated ( $d = 5 \mu\text{m}$ ,  $l = 10\text{--}15 \mu\text{m}$ ), contain many twins and zig-zag forms of GBs. The presence of the zig-zag GBs in ZnO:In ceramics prevents the rapid spread of cracks along GB [21]. Confirmation of this is the fracture transcrystalline mode in In doped ceramics (Fig. 4,c) compared with undoped.

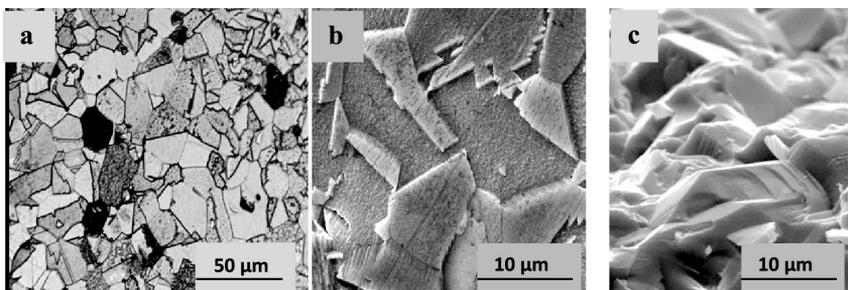


Fig. 4. Micrographs (a) and SEM image (b) of etched external surfaces, SEM image of fracture (c) of sintered 0.13 wt% In doped ZnO ceramics.

Indium induced zig-zag edges of polar (Zn-0001) planes in the nanobelts and ZnO films were observed in [22], [23]. In our case, zig-zag form appearance reflects the evolution of powder interfaces, discussed above, and are associated with the presence of ZnOIn compounds in the local places of GBs, which lead to the different mobility of GB structural elements during sintering [24]. The relative EDS data obtained from fracture surfaces of the ZnO: In samples showed that EDS signals of indium were obtained only in the area with high density of zig-zag and faceted GBs of fine grains, where O/Zn/In ratio is In-0.45, Zn-84.18, O-15.38 (wt%). Stoichiometric ZnO crystal exhibits the ratio O-19.99, Zn -80.3 (wt %) [2]. Therefore, GBs in ZnO:In ceramics have excess amount of Zn and In that confirms the presence ZnOIn compound.

Moreover, zig-zag GBs forms prevent the grain growth [10], [21] that, in turn, promotes the rapid removal of point defects during sintering due to shorter paths of vacancies from the source inside the grain to the sinks at faceted GBs.

This should primarily be reflected in PL results.

### 3.3. Photoluminescence of Ceramics

Figure 5,a,b shows the PL spectra for undoped ZnO and ZnO:In ceramics obtained at 300K. For both investigated ceramics excitonic at  $\lambda = 380 \text{ nm}$  and “green” at  $\lambda = 480\text{--}520 \text{ nm}$  bands PL were observed. These bands are well known for single crystals, nanopowders, coatings and ceramics. Undoped ceramics has the wide “green” (defect associated) band at  $\lambda = 480\text{--}520 \text{ nm}$ , whereas defect associated luminescence in ZnO:In is negligible. The ratio of defect to excitonic intensities at the same time range is an important parameter for ceramic characterization. The calculated values of this parameter  $\alpha = I_{\text{def}}/I_{\text{exc}}$  at 300K are 1.2 and 0.08 for undoped and indium doped ZnO ceramics, respectively. Therefore, the indium doping of ZnO ceramics leads to the decrease of PL  $\alpha$  parameter in 15 times. Here it can be noted that calculated from [14] for 0.13 wt% In doped ZnO ceramics X-ray luminescence parameter  $\alpha$  was even decreased by 85 times compared with undoped.

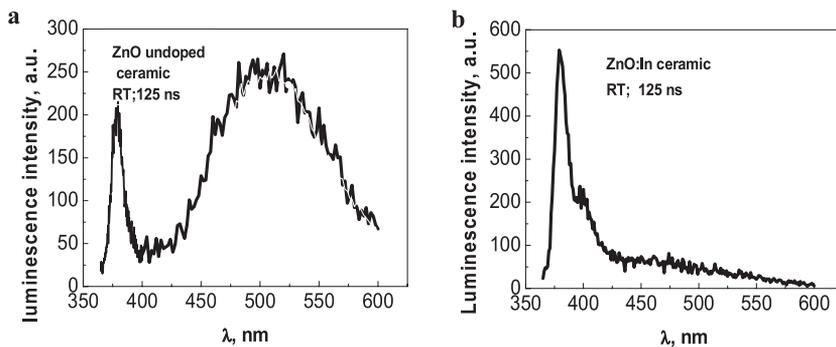


Fig. 5. The photoluminescence spectra of undoped ZnO (a) and ZnO:0.13 %wt In ceramics (b).

In the undoped ZnO ceramics disseminated vacancies remain inside grains due to slow volume diffusion processes at 1150 °C and large distance to probable sinks in the coarse grain microstructure. In the ZnO:In ceramics faceted GBs with the local zig-zag forms contribute to a shorter path of vacancies from the source inside the grain to sink at the boundaries. Thus, the doping of ZnO with 0.13 wt% indium facilitates the elimination of point defects that is very important for a short decay time of scintillators [8].

#### 4. CONCLUSIONS

A comparative analysis showed that doping of ZnO with 0.13 wt% indium changes all investigated properties of ZnO ceramics. During the mixing of powders indium induces a faceting-rounding transition of initially ZnO particles promoting good sintering with formation of diffusion active high angle GBs. This phenomenon is caused by the thermodynamics of In with ZnO contact interaction at the edges of Zn-0001 polar plane, leading to the stable ZnOIn compound formation in local places of GBs. The effect of In doping on the ZnO ceramics microstructure is mainly concerned with modifications of grain boundaries during sintering, including formation of fine grains, faceted GBs with zig-zag forms and excess amount of Zn and In.

Such improved GBs provide reliable ways to remove point defects and significantly reduce the PL parameter  $I_{\text{def}}/I_{\text{exc}}$ . Results characterise 0.13 %wt In doped ZnO ceramics as a prospective material for fast scintillators.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

1. Klingshirn, C. F., Meyer, B. K., Waag, A., & Hoffmann, A. (2010). Zinc oxide. From fundamental properties towards novel applications. *Springer Series in Materials Science. 120*. Springer, Heidelberg.

2. Ozgur, U., Alivov, Y I., Liu, C., Teke A., Reshchikov, M. A., Dogan, S. ... Morkoc, H. (2005). A comprehensive review of ZnO materials and devices. *J. App.Phys.* 98, 043011.
3. Zhang, Z., Du, J., Li, B., Zhang, S., Hong, M., Zhang, X. ...Zhang, Y. (2017). Ultrathin strain gated field effect transistor based on In-doped ZnO nanobelts. *APL Materials* 5, 086111.
4. Lu, K. (2008). Sintering of nanoceramics. *Intern. Mater. Rev.* 53, 21–38.
5. Polyakov, B., Dorogin, L., Lohmus, A., Romanov, A., & Lohmus, R. (2012). In situ measurement of the kinetic friction of ZnO nanowires inside a scanning electron microscope. *Appl. Surf. Sci.* 258, 3227–3231.
6. Wilson, H. F., Tang, C., & Barnard, A. S. (2016). Morphology of zinc oxide nanoparticles and nanowires: Role of surface and edge energies. *Phys. Chem. C*, 120, 9498.
7. Huber, S. E., Hellström, M., Probst, M., Hermansson, K., & Broqvist, P. (2014). Large-scale SCC-DFTB calculations of reconstructed polar ZnO surfaces. *Surf. Sci.* 628, 50–61.
8. Wilkinson, J., Ucer, K.B., & Williams, R.T. (2005). The oscillator strength of extended exciton states and possibility for very fast scintillators. *Nucl. Instr. and Methods. Phys. Res. A* 537, 66–70.
9. Rodnyi, P. A., Chernenko, K. A., Gorokhova, E. I., Kozlovskii, S.S., Khanin, V.M., & Khodyuk, I.V. (2012). Novel scintillation material – ZnO transparent ceramics. *IEEE Trans. Nucl. Sci.* 59(5), 2152–2155.
10. Kelly, J. P., & Graeve, O A. (2013). Effect of powder characteristics on nanosintering sintering mechanisms of convention nanodensification and field assisted processes. *Sintering*, 57–95.
11. Muktepavela, F., Zabels, R., Sursajeva, V., Grigorjeva, L., & Kundzins, K. (2012). The role of nanopowder particle surfaces and grain boundary defects in the sintering of ZnO ceramics. *IOP Conf. Ser. Mater. Sci. Eng.* 38, 012016.
12. Muktepavela, F., Grigorjeva, L., Kundzins, K., Gorokhova, E., &Rodnyi, P. (2015). Structure, nanohardness and photoluminescence of ZnO ceramics based on nanopowders. *Phys. Scr.* 90 094018.
13. Yanagida, T., Fujimoto, Y., Yoshikawa, A., & Maeo, S. (2010). Scintillation properties of In-doped ZnO with different In concentrations. *IEEE Trans. Nucl. Sci.* 57(3), 1325–1328.
14. Gorokhova, E. I., Eron'ko, S. B, Kul'kov, A., Oreshchenko, E. A., Simonova, K. L., Chernenko, K. A. ... Wiczorek, H. (2015). Development and study of ZnO:In optical scintillation ceramic. *J. Opt. Technol.* 82(12), 837–842.
15. Sohn, J. I., Hong, W-K, Lee, S., Lee, S., Ku, J., Park, Y. J. ... Kim, J.M. (2014). Surface energy-mediated construction of anisotropic semiconductor wires with selective crystallographic polarity. *Sci. Rep.* 4, 5680.
16. Klinger, L., & Rabkin, E. (2010). Sintering of fully faceted crystalline particles. *Intern. J. Mater.Res.*, 101 (1), 75–83.
17. Yoon, Y., & Cho, Y., K. (2005) Roughening transition of grain boundaries in metals and oxides. *J. Mater. Sci.*, 40, 861–870.
18. Moriga, T., Edwards, D.D., Mason, T.O., Palmer, G.B., Kenneth Poepfelmeier, R., Schindler, J.L. ... Nakabayashi, I. (1998). Phase Relationships and Physical Properties of Homologous Compounds in the Zinc Oxide–Indium Oxide System. *J. Am. Ceram. Soc.*, 81, 5, 1310-1316.
19. Tang, C., Spencer, M.J. S., & Barnard, A. S. (2014). Activity of ZnO polar surfaces: An insight from surface energies. *Phys. Chem. Chem. Phys.*, 16, 22139–22144.
20. Muktepavela, F., Bakradze, G., & Stolyarova, S. (2006). Effect of mechanoactivation on interfacial interaction in metal/oxide systems. *Defect and Diffusion Forum*, 249, 263–268.

21. Cahn, R. W. (ed.). (1965). *Physical Metallurgy*. 8. Amsterdam: North Holland.
22. Oba, F., Sato, Y., Yamamoto, T., Ohta, H., Hosono, H., & Ikuhara, Y. (2005). Effect of boundary plane on the atomic structure of [0001]  $\Sigma$  7 tilt grain boundaries in ZnO. *J. Mater. Sci.* 40, 3067.
23. Fan, H. J., Fuhrmann, B., Scholz, R., Himcinschi, C., Berger, A., Leipner, H. ... Zacharias, M. (2006). Vapour-transport-deposition growth of ZnO nanostructures: Switch between c-cxial wires and a-axial belts by indium doping. *Nanotechnology*, 17, 231–239.
24. Sursaeva, V, Gornakova, A., & Muktepavela, F. (2014). Grain boundary ridges slow down grain boundary motion: In-situ observation. *Mater. Lett.* 124, 241735.
25. Chen, I-W, & Wang, X.-H. (2000). Sintering dense nanocrystalline oxide without final stage grain growth. *Nature*, 404, 168–171.

## INDIJA IETEKME UZ ZnO PULVERA MORFOLOĢIJU UN MIKROSTRUKTŪRAS EVOLŪCIJU ZnO:In KERAMIKĀ KĀ SCINTILĀTORU MATERIĀLU

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### K o p s a v i l k u m s

Caurspīdīgas ZnO un ZnO:In keramikas izpelnās interesi pielietojumiem augstas efektivitātes scintilatoros. Šim nolūkam nepieciešama augsta fotolumiscences (FL) eksitonu pīķa intensitāte, iespējami vāja ar defektu stāvokļiem saistītā „zaļā” josla ZnO keramikās ar augstu mikrostruktūras kvalitāti. Šajā darbā ar karstās presēšanas pie 1500 °C iegūtas ZnO un ZnO:0,13 wt % In keramikas pētītas, izmantojot SEM, TEM un FL metodes. Noskaidrots, ka jau pulveru sajaukšanas stadijā In veicina sākotnēji fasetēto daļiņu pāreju uz noapaļotu stāvokli, kas sekmē saķepināšanos un liellenķņu graudu robežu (GR) ar lielu difūzijas spēju veidošanos. Indija inducēta keramikas mikrostruktūras evolūcija noved pie fasetētas, vietām zigzaga GR. Šī GR modifikācija bremzē graudu augšanas procesu, nodrošinot noteces vietas punktvieda defektiem un FL parametra  $\alpha = I_{\text{def}}/I_{\text{exc}}$  (attiecība starp defektu un eksitonu FL intensitāti) ievērojamu samazināšanu, salīdzinot ar nedopeto ZnO keramiku. Rezultāti liecina, ka ZnO:0.13 wt%In keramiku ar uzlabotām GR var izmantot kā materiālu scintilatoriem.

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