

HYDROTHERMAL PREPARATION OF OXIDE (Ga₂O₃, ZnO, TiO₂) AND DERIVATIVE NANOPARTICLES E. Rusu¹, V. Morari¹, T. Guțul¹, V. Ursaki², and P. Vlazan³

¹National Center for Materials Study and Testing, Technical University of Moldova, 2004 Chisinau, Moldova

¹Institute of Electronic Engineering and Nanotechnologies "D. Ghitu", 2028 Chisinau, Moldova ¹National Center for Materials Study and Testing, Technical University of Moldova, 2004 Chisinau, Moldova

³National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, 300569, Romania

https://doi.org/10.53081/mjps.2022.21-1.06

Abstract

A brief review of our recent research on preparation and characterization of oxide nanoparticles and their derivatives by hydrothermal growth is presented. A series of Ga_2O_3 , ZnO, and TiO₂ nanoparticles, as well derivative nanomaterials including GaN nanowires and ZnO/TiO₂ nanocompostes have been prepared. Ga_2O_3 and ZnO nanopowders have been produced using metal nitrate hydrates as precursors, while Titanium isopropoxide was used for preparation of TiO₂ nanopowders. GaN nanowires have been produced by nitridation of Ga_2O_3 nanomaterials. The produced nanomaterials have been characterized scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis and Fourier transform infrared (FTIR) spectroscopy. Ga_2O_3 nanoparticles doped with Eu³⁺ ions have been characterized by photoluminescence spectroscopy in order to assess their prospects in developing nanophosphors materials.

Keywords: hydrothermal synthesis; precursors; nanopowders; nanowires; crystal structure; vibration modes; photoluminescence; nanophosphors.

Rezumat

A brief review of our recent research on preparation and characterization of oxide nanoparticles and their derivatives by hydrothermal growth is presented. A series of Ga_2O_3 , ZnO, and TiO₂ nanoparticles, as well derivative nanomaterials including GaN nanowires and ZnO/TiO₂ nanocompostes have been prepared. Ga_2O_3 and ZnO nanopowders have been produced using metal nitrate hydrates as precursors, while Titanium isopropoxide was used for preparation of TiO₂ nanopowders. GaN nanowires have been produced by nitridation of Ga_2O_3 nanomaterials. The produced nanomaterials have been characterized scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis and Fourier transform infrared (FTIR) spectroscopy. Ga_2O_3 nanoparticles doped with Eu^{3+} ions have been characterized by photoluminescence spectroscopy in order to assess their prospects in developing nanophosphors materials.

Cuvinte cheie: sinteză hidrotermală; precursori; nanopulbere; nanofire; structură cristalină; moduri de vibratie; photoluminescență; nanofosfori.

1. Introduction

Hydrothermal method is one of the most suitable techniques in the growth of a wide range on nanomaterials and nanocomposites, because it requires moderate synthesis temperature, it is low-cost, simple and environmental friendly [1]. At the same time, the hydrothermal process ensures obtaining of particles with reduced agglomeration, narrow particle size distribution, good phase homogeneity and controlled particle morphology and structure with high reproducibility [2,3]. These nanostructures parameters can be tuned by a variation of the temperature, pressure, reaction time, nature, and concentration of precursors in solutions [4].

Among nanomaterials prepared by hydrothermal method, metal oxide materials are widely present, and nitrate hydrates are among the preferred precursors used in their synthesis [5].

Metal nitrate hydrates with Zn, Mn, Fe, Ce, Y. Co, Al, Eu, Cu, etc have been employed in hydrothermal synthesis of nanomaterials [5]. Metal oxides form different compounds and crystalline structures, which properties could vary widely from insulators to superconductors, resulting in a wide variety of potential applications [6]. Particularly, $Ga(NO_3)_3 \cdot nH_2O$ and $Zn(NO_3)_3 \cdot nH_2O$ were used for the production of gallium oxide (Ga_2O_3) and zinc oxide (ZnO) nanostructures. The combination of these two metal nitrate hydrates proved to be very efficient in doping ZnO nanostructures with Ga over a broad range of concentrations [7].

Many oxide-based electrocatalysts, including Ga_2O_3 nanostructures have been used for water splitting and removal of volatile organic compounds [8-10]. Apart from that, Ga_2O_3 nanostructures have been demonstrated in applications such as gas sensors, solar cells, photodetectors and other optoelectronic applications due to their wide bandgap energy and good luminescence properties [11-13].

ZnO is another materials widely employed in nanostructures prepared by hydrothermal synthesis, which are used in photocatalysis, energy harvesting and electronics, due to unique properties including high surface to volume ratio, nontoxicity, biocompatibility, chemical and photochemical stability, optical transparency, and electrochemical activity [3,14]. Apart from that, ZnO nanoparticles are used in textiles due to their UV blocking properties, in sterilizing surroundings due to their antibacterial and antifungal activities, in cosmetics, food packaging, and biomedical applications [4,15].

ZnO material is also considered a preferred alternative to TiO_2 in some applications, including those of electron transport layer in perovskite solar cell, because it possesses energy levels and physical properties similar to those of TiO_2 , but requires lower temperatures for processing from solutions to achieve structures of different morphologies [16]. TiO_2 requires high processing temperature to achieve highly crystalline layers. In spite of that, TiO_2 is an important material for applications in solar cells, ultra-thin capacitors, optical devices, gas and chemical sensors, biomedical and self-cleaning coatings, and photocatalysis [2-19]. Apart from that, TiO_2 is widely used as pigment in paints, printing inks, cosmetics, papers, plastics, rubber etc. [20,21].

Various precursors were proposed for producing TiO_2 nanostructures by hydrothermal synthesis [21], including titanium butoxide ($Ti(OBu)_4$) [2,18,22,23,24], titanium tetrachloride ($TiCl_4$) [20], titanium tetraisopropoxide (TTIP) [17], and TiO_2 powders including Degussa P25 [19,25].

Apart from monophasic nanomaterials, composite nanostructures have been recognized as

important materials for a series of applications. TiO_2 nanorods decorated with CeO₂ nanoparticles have been produced by hydrothermal synthesis with titanium butoxide precursor, and their UV filtering applications have been demonstrated [23]. A Ga₂O₃/TiO₂ nanocomposite has been prepared with Ga (NO₃)₃·H₂O and TiCl₃ precursors as efficient photocatalyst with excelent biocompatibility, demonstrated particularly with respect to the Human embryonic kidney. The antibacterial activity against bacillus subtilis and staphylococcus aureus of this composite was demonstrated [26].

In this paper, we present a brief review of our research on preparation and characterization of oxide nanoparticles and their derivatives by hydrothermal growth.

2. Experimental

Since, according to literature data, metal nitrate hydrates are the most preferred precursors in hydrothermal synthesis of nanomaterials, the research in this paper was focused on using $Ga(NO_3)_3 \cdot 9H_2O$ and $Zn(NO_3)_3 \cdot 6H_2O$ in the hydrothermal preparation of Ga_2O_3 and ZnO nanoparticles, respectively. 2.5M high purity gallium nitrate or zinc nitrate from Sigma-Aldrich was dissolved in 50 ml of distilled water, and the pH of the solution was adjusted to the value of 9 by means of the 1M NaOH solution under vigorous magnetic stirring. The solutions were subsequently transferred in a teflon autoclave with a steel shell and treated for several hours at the temperature of 220 °C. After autoclaving the nanopporticles were separated by settling and filtering with a subsequent drying in an oven during 2 hours at 80°C. Titanium isopropoxide was used as precursor for the preparation of TiO₂ nanoparticles. 2 mL of this precursor was added to a solution composed of 0.2g of polyvinyl alcohol and 50 ml of ethanol. The mixture was stirred during 1 hour and introduced subsequently into an autoclave, where it was treated at 220 °C during 2 hours. After autoclaving the nanopporticles were separated by settling and filtering with a subsequent drying the nanopporticles were separated by settling and filtering with a subsequently into an autoclave, where it was treated at 220 °C during 2 hours. After autoclaving the nanopporticles were separated by settling and filtering with a subsequent drying in an oven during 2 hours at 80°C.

The morphology and chemical composition microanalysis of the produced films were studied using a TESCAN TS 5130MM scanning electron microscope equipped with tools for energy dispersive X-ray analysis (EDX). X-ray diffraction (XRD) measurements were carried out using the PANalytical X'Pert Pro MPD diffractometer with CuK α radiation ($\lambda = 1.54$ Å). Fourier transform infrared (FTIR) spectra were measured with a spectrometer from Perkin Elmer. The PL spectra were excited by the 405 nm line of a mercury lamp at room temperature, and measured with a SDL-1 spectrometer.

3. Results and Discussion

The scanning electron microscope (SEM) image of powders produced with a 5 hours hydrothermal process is shown in Fig. 1. One can see that the morphologies of the obtained powders are quite different. The TiO₂ powder is composed of spherical nanoparticles with sizes from several hundreds of nanometers to 1 μ m. The morphology of the ZnO powder is more complex, it consisting of nanoparticles with sizes of (100 – 200) nm agglomerated in formations of several micrometers. The Ga₂O₃ powder represents elongated nanoparticles with the length up to 1 μ m and the transversal dimensions around several hundreds of nanometers.



Fig. 1. SEM images of TiO₂ (a), ZnO (b), and Ga₂O₃ (c) powder produced with 5 hours hydrothermal process.

With increasing of the duration of the hydrothermal process from 5 hours to 24 hours, the elongated Ga_2O_3 nanoparticles are transformed into nanowires with the length of several tens of micrometers as illustrated in Fig. 2b.

Apart from oxide nanoparticles, derivative structures have been prepared. GaN nanowires have been produced from Ga_2O_3 nanocrystals. The transformation of the Ga_2O_3 nanowires into GaN ones was performed in a horizontal tube furnace with a quartz boat under flowing ammonia with a subsequent nitridation in a mixture of NH₃ and H₂ with flow rates of 0.35 and 2.5 l/min, respectively. The quartz boat was heated at temperature of 900-950 °C during 90-150 minutes, and cooling down occurred in a natural fashion after the furnace was switched off. The initial morphology of Ga_2O_3 nanowires was preserved upon their transformation into GaN, as illustrated in Fig. 2c.



Fig. 2. SEM images of Ga_2O_3 nanoparticles produced with 5 hours (a) and 24 hours (b) hydrothermal process, as well as of GaN nanowires produced from Ga_2O_3 ones (c).

The results of XRD spectroscopy demonstrated the presence of a single β -Ga₂O₃ phase after the hydrothermal process (Fig. 3a), while the diffraction peaks observed in the XRD pattern of the material produced by nitridation correspond to a hexagonal wurtzite GaN structure (Fig. 3b). The XRD pattern indicates on the high crystallinity of GaN nanoparticles with the mean sizes around 30 nm, as deduced from the Sherrer formula. Since the length of GaN nanowires is of several tens of micrometers and their diameter is of (0.5 – 2) µm (see Fig. 2c), one can conclude that the GaN nanowires are composed of smaller crystallites.



Fig. 3. XRD pattern of Ga₂O₃ nanoparticles obtaining by hydrothermal method (a) and GaN nanowires produces after nitridation (b).

Apart from TiO₂ and ZnO nanoparticles, a derivative composite material was produced according to a technological route with a 3 mM $Zn(NO_3)_2 \cdot 6H_2O$ precursor dissolved in a solution of 3 mM urea. The precipitation of the composite material was performed in a solution of 1M NaOH with the addition of 2 ml of titanium isopropoxide and 10 ml of ethylic alcohol. The obtained suspension was continuously stirred during 1 hour at 65 °C. The obtained precipitate was filtered, washed several times in distilled water and ethylic alcohol, dried in an oven at 80 °C during 2 hours, and subjected to calcination at 500 °C during 4 hours.

Figure 4 presents XRD spectra of the composite material as compared to spectra of pure ZnO and TiO₂ powders. The pattern of the TiO₂ powder is referenced to the anatase structure (00-001-0562 JCPDS card), with peaks at 2 Θ equal to 25.5, 37.9, 48.1, 53.9, 55.3, 62.6, 68.8 and 70.5 degrees, corresponding to (101), (004), (200), (105), (211), (204), (116) and (200) reflexes, respectively, while that of the ZnO powder is indexed to a wurtzite structure (01-079-0205 JCPDS card), with peaks at 32, 35, 37, 48, 57, 63, 67, 68, and 69 degrees, correspond to the (100), (002), (101), (102), (110), (103), (200), (112), and (201), reflexes, respectively. All the observed Bragg reflections from the ZnO powder are consistent with Wurtzite's P63mc space group. Diffraction peaks related to both wurtzite ZnO and anatase TiO₂ nanocrystallites appear in the XRD pattern of ZnO/TiO₂ nanocompostes. At the same time, additional peaks associated with the rutile phase of TiO₂ are observed at $2\theta = 35.6$ and 62.0° (JCPDS no. 76- 0324). The sizes of nanoparticles composing the TiO₂ powder are in the range of 10-20 nm according to the Scherrer formula, while those of particles constituting the ZnO powder are in the range of 30-80 nm. Since the sizes of TiO₂ and of ZnO particles deduced from Figs. 1a and 1b are much larger, similarly to GaN nanowires one can conclude that these particles are composed of smaller crystallites.



Fig. 4. XRD spectra of ZnO and TiO₂ powders as well as the ZnO/TiO₂ nanocomposite

The formation of β -Ga₂O₃ nanoparticles was also confirmed by the analysis of FTIR spectrum in Fig. 5b. It is known that the metal oxides exhibit absorption bands under 1000 cm⁻¹ related to inter-atomic Me-O or Me-O-Me vibrations [27]. The spectrum is dominated by the absorption bands at 455 cm⁻¹ and 684 cm⁻¹, previously assigned to vibration modes of the Ga-O bonds in the β -Ga₂O₃ structure (A_u modes) [28], while the other peaks observed at 528 cm⁻¹, 624 cm⁻¹, 748 cm⁻¹ have been related to B_u modes. At the same time, no absorption bands related to the Ga₂O₃ phase are observed in the FTIR spectrum of GaN nanowires (Fig. 5a), their spectrum being dominated by two absorption bands at 565 cm⁻¹ and 634 cm⁻¹. The first band has been previously attributed to the Ga–N stretching vibration in the hexagonal type GaN crystals (E₁(TO) mode) [29], while the second one may be related to a local vibration mode (LVM) attributed to nitrogen and gallium vacancies.



Fig. 5. FTIR spectra of GaN nanowires (a), Ga_2O_3 nanoparticle (b), TiO_2 nanoparticles (c), and TiO_2/ZnO nanocomposite (d).

In addition to Me-O vibrations, absorption band related to bonds involving C atoms in compounds adsorbed at the surface of the prepared oxide nanomaterials have been observed. The vibrations observed at 1067cm⁻¹ and 1987 cm⁻¹ in the TiO₂/ZnO nanocomposite (Fig. 5d) can be attributed to C=O stretching vibrations in carboxylic acids and other carboxylic compounds present on the nanocomposite surface. The absorption band at 1252 cm⁻¹ may be associated with C-O stretching vibrations in alcohols or ethers, while the bands at 1401 and 1460 most probably are related to OH group bending vibrations in alcohols or carboxylic acids. The band at 1640 cm⁻¹ can be attributed to C=O bending vibrations. The absorption bands observed at 2160 cm^{-1} and 2304 cm⁻¹ in the TiO₂/ZnO nanocomposite, as well as the band observed at 2311 cm⁻¹ in TiO₂ nanoparticles can be attributed to stretching vibrations of CO₂ absorbed from atmosphere on the materials surface. The absorption bands observed at 3895 cm⁻¹ and 2997 cm⁻¹ in the TiO₂/ZnO nanocomposite, as well as the bands observed 2910 cm⁻¹ and 2981 cm⁻¹ in TiO₂ nanoparticles are usually associated with C-H stretching vibrations in organic compounds, and their exact position depends upon the hybridization state of the carbon. The higher energy bands in the range of 3000 - 3800 cm⁻¹, including the broad bands can be attributed to vibrations of the OH group in water on the metal oxide surface [30].

The prepared nanomaterials are expected to be prospective for photocatalytic, antibacterial and antifungal applications, as well as for biosynthesis of fungal proteases and production of enzyme preparations [31-34]. With the purpose of assessing their prospects in phosphors preparation, they were doped with Eu^{3+} ions, and their luminescence properties have been investigated. For doping Ga₂O₃ nanopowder with Eu^{3+} ions, EuCl₃ with concentration from 0.3 to 3 at% was added to the 0.05M Ga(NO₃)₃ solution in the hydrothermal synthesis. The pH of the solution was adjusted to the value of 9.5 by adding 25% of NH₄OH under additional stirring for 30 minutes, before introducing the obtained suspension in the autoclave.

The PL spectrum of a Ga₂O₃ nanopowder doped with a 2% concentration of Eu is shown in Fig. 6a. Since the quantum energy of the excitation light with wavelength of 405 nm is lower than the β - Ga₂O₃ bandgap, most probably the luminescence is excited by an intra-central transition in the Eu³⁺ ions, while all the observed emission lines are consistent with the ⁵D₀ \rightarrow ⁷F_j (J = 1,2,3,4) intra-central transitions, where J = 1 is for the PL band at 585 nm, J = 2 is for the lines at 606-818 nm, J = 3 is for lines around 650 nm, and J = 4 is for lines in the spectral range of (680 – 710) nm.



Fig. 6. (a) PL spectrum of Ga₂O₃ nanoparticles doped with Eu³⁺ ions obtaining by hydrothermal method; (b) a comparison of spectra of samples prepared by hydrothermal method (curve 1) and solid phase reactions (curve 2) [35].

The multiplets within these PL bands are determined by the local symmetry of sites where Eu^{3+} ions are incorporated into the β -Ga₂O₃ monoclinic lattice with the space group C2/m. It is supposed that the Eu^{3+} ions occupy the sites of Ga^{3+} ions with either tetrahedral or octahedral crystallographic coordination. Therefore, the local symmetry of Eu^{3+} ions should be T_d or O_h , respectively. However, since the ionic radii of the Ga³⁺ ions are 0.047 nm and 0,062 nm for the tetrahedral and octahedral coordination, respectively [36,37], and the ionic radius of Eu³⁺ ions is 0.095 nm, it is expected that the octahedral site is more suitable for Eu^{3+} ions. On the other hand, the large difference in the ionic radii of Eu³⁺ and Ga³⁺ ions implies that the octahedrons are disported, and the local symmetry of the sites where Eu^{3+} ions are incorporated should be lowered to the C_s symmetry [38]. The incorporation of Eu³⁺ ions in sites with such symmetry was previously confirmed in β-Ga₂O₃ doped with Eu and annealed at 1100 °C [39]. The presence of emission lines associated with crystal field levels of Eu³⁺ ions in the spectrum of the sample prepared by hydrothermal synthesis indicates on the good crystalline quality. The advantage of the hydrothermal synthesis over the solid phase reaction method is evidenced from the comparison of the PL spectra of samples prepared by these two technologies (Fig. 6b). One can see that the spectrum of the sample prepared by solid phase reaction is characterized by broader PL bands resulting from superimposing lines, which are usually observed in amorphous materials

and glasses.

The incorporation of Eu^{3+} ions was also demonstrated in the wurtzite lattice of GaN nanowires produced by nitridation of Ga₂O₃ powders prepared by hydrothermal synthesis.

4. Conclusions

The results of this study demonstrated that Ga_2O_3 , ZnO, and TiO₂ nanoparticles, as well derivative nanomaterials, including GaN nanowires and ZnO/TiO₂ nanocompostes, with high crystalline quality can be produced by hydrothermal synthesis as a low cost technology. Metal nitrate hydrates and titanium isopropoxide are suitable and accessible precursors for this purpose. The morphology of the produced nanomaterial can be controlled by choosing the duration of the hydrothermal process. The luminescence characterization of Ga_2O_3 nanoparticles doped with Eu^{3+} ions demonstrated efficient incorporation of the Eu^{3+} ions into the β -Ga₂O₃ crystal lattice, therefore opening prospects for the development of nanophosphors on the basis of these nanomaterials.

Acknowledgments. This research was funded by National Agency for Research and Development of Moldova under the Grants #20.80009.5007.02.

References

- [1] N. U. Saidin, T. F. Choob, and K. Y. Kokc, IOP Conf. Ser.: Mater. Sci. Eng . 298, 012016 (2018).
- [2] M. Rehan, X. Lai, and G. M. Kaleb, CrystEngComm 13, 3725 (2011).
- [3] A. I. B. Rovisco, R. Branquinho, J. V. Pinto, R. Martins, E. Fortunato, and P. Barquinha. In *Novel Nanomaterials*, ed. K. Krishnamoorthy, IntechOpen 2021, Chapter 1. <u>http://dx.doi.org/10.5772/intechopen.94294</u>
- [4] F. Demoisson, R. Piolet, and F. Bernard, Cryst. Growth Des. 14, 5388 (2014).
- [5] H. Hayashi and Y. Hakuta, Materials 3, 3794 (2010).
- [6] Y. Quan, D. Fang, X. Zhang, S. Liu, and K. Huang, Mater. Chem. Phys. 121 142 (2010).
- [7] P Gaffuri, E. Appert, O. Chaix-Pluchery, L. Rapenne, M. Salaün, and V. Consonni, Inorg. Chem. 58, 10269 (2019).
- [8] H. Gao, M. Yang, X. Liu, X. Dai, Xi. Q. Bao, and D. Xiong. Frontiers of Optoelectronics 15, 8 (2022).
- [9] S. Kim, H. Ryou, I. G. Lee, M. Shin, B. J. Cho, and W. S. Hwang, RSC Adv. 11, 7338 (2021).
- [10] H. Ryou, T. H. Yoo, Y. Yoon, I. G. Lee, M. Shin, J. Cho, B. J. Cho, and W. S. Hwang, ECS J. Solid St. Sci. Technol 9, 045009 (2020).
- [11] L. S. Reddy, Y. H. Ko, and J. S. Yu, Nanoscale Res. Lett. 10, 364 (2015).
- [12] L. Cui, H. Wang, B. Xin, and G. Mao, Appl. Phys. A 123, 634 (2017).
- [13] M. Hirano, K. Sakoda, and Y. Hirose, J Sol-Gel Sci Technol 77, 348 (2016).
- [14] C. Yilmaz and U. Unal, , Appl. Surf. Sci. 368, 456 (2016).
- [15] B. Bulcha, J. L. Tesfaye, D. Anatol, R. Shanmugam, L. Priyanka Dwarampudi, N. Nagaprasad, V. L. Nirmal Bhargavi, and R. Krishnaraj, J. Nanomaterials 2021, 8617290 (2021).
- [16] K. Sekar, R. Nakar, J. Bouclé, R. Doineau, K. Nadaud, B. Schmaltz, and G. Poulin-Vittrant.

Nanomaterials 12, 2093 (2022).

- [17] S.-P. Hong, J. Park, S. S. M. Bhat, T. H. Lee, S. A. Lee, K. Hong, M.-J. Choi, M. Shokouhimehr, and H. W. Jang, Cryst. Growth Des. 18, 11, 6504 (2018).
- [18] S. Dey and S. C. Roy, Nano Ex. 2, 010028 (2021).
- [19] B. G. T. Keerthana, T. Solaiyammal, S. Muniyappan, and P. Murugakoothan, Materials Lett. 220, Pages 20 (2018).
- [20] E. Y. C. Yan, S. Zakaria, C. H. Chia, AIP Conf. Proc. 1614, 122 (2014).
- [21] T. Gupta, Samriti, J. Cho, and J.Prakash, Mater. Today Chem. 20, 100428 (2021).
- [22] M. Tang, Y. Xia, D. Yang, J. Liu, X. Zhu, R. Tang, Materials (Basel) 14, 5674 (2021).
- [23] A. Morlando, J. McNamara, Y. Rehman, V. Sencadas, P. J. Barker, and K. Konstantinov, J. Mater. Sci. 55, 8095 (2020).
- [24] A. Prathan, J. Sanglao, T. Wang, C. Bhoomanee, P. Ruankham, A. Gardchareon, and D. Wongratanaphisan, Sci. Rep. 10, 8065 (2020).
- [25] M. A. L. Zavala, S. A. L. Morales, and M. Avila-Santos, Heliyon 3, e00456 (2017).
- [26] M. Ramesha, A. Gangadhar, M. Chikkamadaiah, and S. Shivanna, J. Photochem. Photobiol. 6, 100020 (2021).
- [27] H. Kumar and R. Rani, Int. Lett. Chem., Phys. Astron. 14, 26 (2013).
- [28] L. Mazeina, Y. N. Picard, and S. M. Prokes, Cryst. Growth Des. 9, 1164 (2009).
- [29] J. H. Boo, C. Rohr, and W. Ho, J. Crystal Growth 189/190, 439 (1998).
- [30] H. Becker, W. Berger, *et.al.*, *Chimie organica practica*, Ed. Stiintifica si Enciclopedica, Bucuresti, pp. 114-115, 1982.
- [31] E. Rusu, V. Ursaki, S. Raevschi, P. Vlazan, Proc. SPIE 9258, Advanced Topics in Optoelectronics, Microelectronics, and Nanotechnologies VII, 92581U (2015), doi: 10.1117/12.2069969.
- [32] E. Rusu, V. Ursaki, I. Culeac, S. Raevschi, and P. Vlazan, 5th Int. Conf. Telecommunications, Electronics and Informatics ICTEI 2015, Chisinau, Moldova, pp. 185 (2015).
- [33] E. Rusu, V. Ursaki, T. Gutul, P. Vlazan, and A. Siminel, In: 3rd Int. Conf. Nanotechnol. Biomed. Engineer. IFMBE Proceedings, eds. V. Sontea and I. Tiginyanu, vol 55. pp 93–96, Springer, Singapore (2015) doi.org/10.1007/978-981-287-736-9_22.
- [34] P. Vlazan, D. H. Ursu, C. Irina-Moisescu, I. Miron, P. Sfirloaga, and E. Rusu, Mater. Character. 101, 153 (2015).
- [35] E. Rusu, V. Ursaki, M. Vasile, and I. Grozescu, J.Optoelectron. Adv. Mater.-Sympozia 1, 59 (2009).
- [36] W. Y. Shen, M. L. Pang, J. J. Lin, and J. Fang, J. Electrochem. Soc. 152, H25 (2005).
- [37] R. D. Shannon, Acta Crystallogr. Sect. A 32, 751 (1976).
- [38] S. Geller, J. Chem. Phys. 33, 676 (1960).
- [39] E. Zhu, R. Li, W. Luo, and X. Chen, Phys. Chem. Chem. Phys. 13, 4411 (2011).