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Research Article

The Optical Properties of Crystalline $Zn_3Nb_2O_8$ Nanomaterials Obtained by Hydrothermal Method

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The present study is focused on the obtaining of the $Zn_3Nb_2O_8$ nanomaterial using the hydrothermal method and its characterization through different techniques. X-ray diffraction at room temperature revealed that a novel crystalline form of the nanomaterial forms at 1100°C belonging to monoclinic space group C2/c. Field-emission scanning electron microscopy evidenced the columnar morphology of the particle's agglomeration and the high resolution electron transmission microscopy confirms the measured interplanar distances calculated from the X-ray diffraction experiments. Using the UV-VIS spectrum and Kubelka-Munk equations, the absorbance and the band gap for the $Zn_3Nb_2O_8$ nanomaterial were calculated. PL spectrum reveals a single peak at 465 nm corresponding to the blue color fluorescence. The novel crystalline nanomaterial might find applications in fluorescence covering of technical devices, due to its capacity to preserve blue fluorescence both in acrylic based paint and after embedding in isopropyl alcohol.

1. Introduction

Considerable attention was gained in the latest years by the light-emitting materials and the lighting technology and the researches were focused to produce low cost inorganic, organic, or hybrid materials capable of exhibiting fluorescence in different colors [1–5].

$Zn_3Nb_2O_8$ has been reported as being an excellent dielectric [6–8] and a good microwave material due to its high quality factor [9, 10] and it can be used for applications in the high frequency domains [6–8]. Its demanded properties consist of resonance frequency in narrow temperature range [6], a high dielectric quality factor [11], and high dielectric constant [6]. The dielectric properties strongly depend on the microstructure organization and of the chemical composition of the material. The density and the particle sizes of the materials should be taken into account in order to obtain the maximum of the dielectric properties [10].

$Zn_3Nb_2O_8$ represents one of the three phases of the ZnO-N_2O_5 system beside ZnN_2O_6 and $Zn_2Nb_{34}O_{87}$ [6, 7, 12, 13]. The reported literature methods for obtaining $Zn_3Nb_2O_8$ refer only to solid state mixed oxide method [6, 10, 14–17] using as precursors ZnO and N_2O_5 and the coprecipitation method performed simultaneously with Eu^{3+}/Dy^{3+} doping [18]. This pseudobinary oxide was also obtained as a secondary phase of the ZnO phase (when trying to obtain ZnO ceramics doped with Nb) and affected the thermoelectric properties of the material (increasing the electrical conductivity and decreasing the Seebeck coefficient) [1].

The main aim of this paper is to present the results regarding the obtaining of the $Zn_3Nb_2O_8$ nanomaterial using the hydrothermal method that allows for the first time generating crystalline self-assembled columnar nanomaterials. The structural and optical properties of the nanomaterial were investigated through different techniques and its blue fluorescence was demonstrated to be preserved both in

isopropyl alcohol and in acrylic based paint, starting the possibilities of novel applications in fluorescence coatings.

2. Experimental

The $Zn_3Nb_2O_8$ nanomaterial was obtained by the hydrothermal method. The starting materials used during the synthesis of $Zn_3Nb_2O_8$ were as follows: niobium (V) oxide, Nb_2O_5 (99%, Merck), and zinc oxide, ZnO (99%, Merck), in a molar ratio of 1 : 3. The pH of the obtained mixture was adjusted by using sodium hydroxide (NaOH) solution of 10 M concentration. The pH value for the synthesis was fixed at 9. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and then was introduced in an oven at 240°C for 24 h. The filling degree of the used autoclave was set at 80%. The resulting white precipitate was filtrated and then washed six times with distilled water and, finally, washed for four times with ethylic alcohol. In the next stage, the precipitate was dried in the oven at 100°C for 4 h.

The characterizations using the room temperature and 1100°C have been performed on well-crystallized powder samples of $Zn_3Nb_2O_8$. The phase identification of the synthesized powders was performed using X-ray diffraction (XRD) with monochromatic Cu Kα ($\lambda = 1.5418$ Å) incident radiation on an X'pert Pro MPD X-ray diffractometer equipped with the X'celerator detector and a high temperature attachment HTK 2000 MSW chamber. Diffraction data were obtained for the angular range $2\theta = 10$–80° using a 0.02° step and the counting time was 5 s. After identifying the phases, the mixture of oxides was afterwards thermally treated at 1100°C for 6 h soaking time. The heating and cooling rate of the heated furnace was set at 5°C/min.

The morphology and the particle's dimension of the sample were investigated by field-emission-scanning electron microscopy (SEM) (Model INSPECT S) and transmission electron microscopy with high resolution transmission microscope (HRTEM) (TITAN G2 80–200). The band gap of the $Zn_3Nb_2O_8$ materials was calculated by recording the diffuse reflectance spectrum at room temperature, using a UV-VIS-NIR spectrometer Lambda 950. The PL spectra were recorded with an Edinburgh Instruments FLS980 luminescence spectrometer, by using a special holder for powder solid samples.

Besides all these investigations, the $Zn_3Nb_2O_8$ nanomaterial was embedded in an acrylic based paint and also in isopropyl alcohol in order to prove its blue fluorescence. The suspensions were allowed to dry in air and were then illuminated with an UV light lamp ($P = 30$ W, $\lambda = 254$ nm).

3. Results and Discussion

3.1. Structural Characterization. The XRD patterns of $Zn_3Nb_2O_8$ (Figure 1) revealed that the novel crystalline phase of the nanomaterial starts forming around 800°C and the maximum of this phase is set around 1100°C. The spectra were compared and indexed with the 01-079-1164 JCPDS. $Zn_3Nb_2O_8$ is monoclinic with the space group C2/c (space group number 15), with the following lattice parameters: $a = 19.093$ Å, $b = 5.927$ Å, $c = 5.220$ Å, and $\alpha = \beta = \gamma = 90^\circ$ and the interplanar distance $d = 2.734$ Å. The mean crystallite size of the $Zn_3Nb_2O_8$ was calculated using Scherrer's formula [19]. The average crystallite size determined from XRD line broadening was found to be 32 nm.

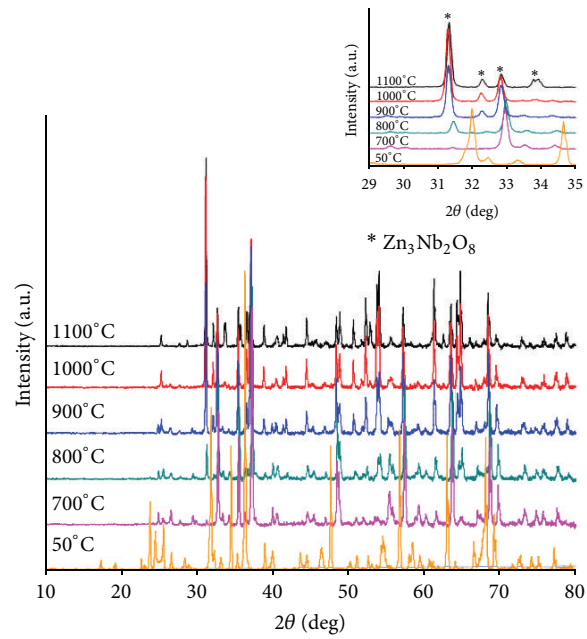


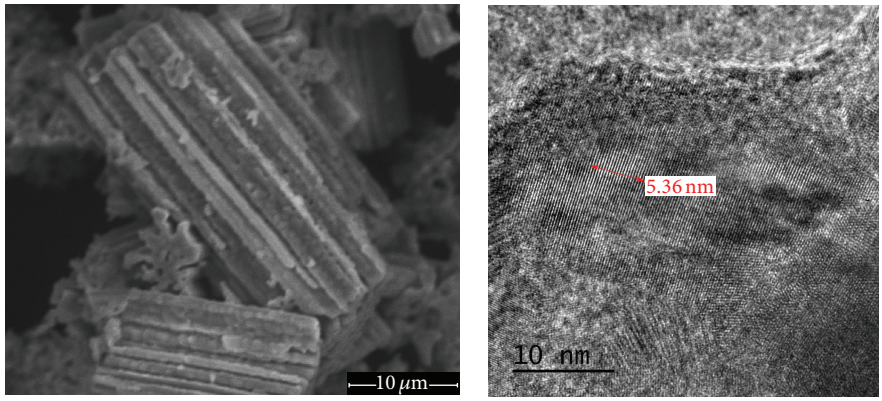
FIGURE 1: XRD patterns of $Zn_3Nb_2O_8$. A magnified zone of the XRD patterns containing the most intense peak was inserted.

In the XRD spectrum, the most intense peak appears at $2\theta = 31.25^\circ$ (-511). In the right upper corner of Figure 1 is presented the magnified image of the most intense peak of the XRD pattern.

3.2. Morphological Characterization. In Figure 2(a), the morphology of the $Zn_3Nb_2O_8$ material can be observed. The agglomerates formed by the $Zn_3Nb_2O_8$ nanomaterial particles are crystallizing as multifacet columns which is a novelty.

Using the high resolution electron transmission microscopy (HRTEM), in Figure 2(b), the forming of the crystallographic planes of the $Zn_3Nb_2O_8$ nanomaterial can be observed. The crystalline plane with Miller indices (-511) indicates the perfect orientation of the lattice. The measured interplanar distance is about 2,68 Å and corresponds to the measurements determined by the X-ray diffraction.

3.3. Optical Properties. The optical absorption spectra (Figure 3) of the $Zn_3Nb_2O_8$ nanomaterial were performed in the 240–480 nm range, at ambient conditions. The absorbance was calculated from the reflectance using Kubelka-Munk equation [20, 21]. From each of the absorption spectra, the $\{(k/s)h\nu\}^2$ versus $h\nu$ was plotted (Figure 3, right upper corner), where k denotes the absorption coefficient, "s" is the scattering coefficient, and $h\nu$ is the photon energy.



(a) (b)

Figure 2: The morphology of $Zn_3Nb_2O_8$: (a) SEM micrographs; (b) HRTEM.

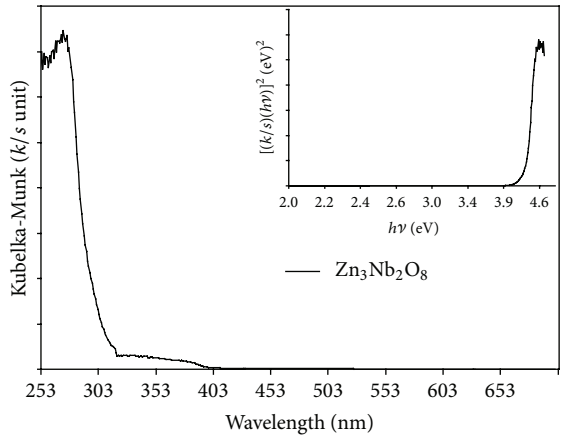


Figure 3: The absorption spectra of $Zn_3Nb_2O_8$. Plot of $\{(k/s)h\nu\}^2$ versus $h\nu$ (energy) of $Zn_3Nb_2O_8$.

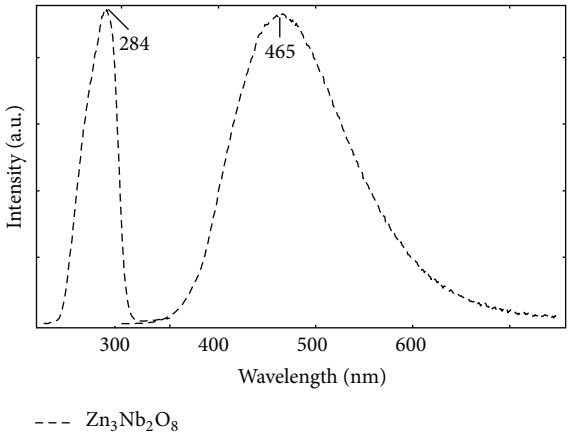


Figure 4: The room temperature PL spectra (excitation at 284 nm and emission at 465 nm) of the synthesized nanomaterial $Zn_3Nb_2O_8$.

The band gap was calculated from Figure 3 (absorbance) and its value was found to be 4.3 eV for $Zn_3Nb_2O_8$.

The PL spectra recorded in the 220–700 nm range for $Zn_3Nb_2O_8$ are presented in Figure 4. The PL spectra show only a single peak at 465 nm for $Zn_3Nb_2O_8$ which is corresponding to the blue color fluorescence.

To point out the blue emitting color of the $Zn_3Nb_2O_8$, in relation to our further interest to exploit this property, a sample of the nanomaterial was embedded in an acrylic based paint and another sample was embedded in isopropyl alcohol. After drying, these two samples were exposed to a UV light lamp (λ = 254 nm). In Figure 5 are presented the images for these two samples that both preserved the initial blue fluorescence of the nanomaterial.

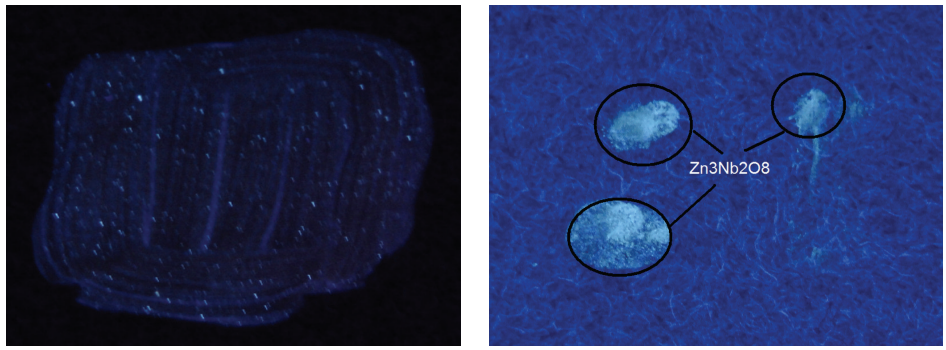
4. Conclusions

In this paper are presented the results regarding the obtaining of the $Zn_3Nb_2O_8$ using the hydrothermal method, in a novel crystalline phase (multifacet columnar crystals) and the characterization of the nanomaterial. The powder structure was established by XRD diffraction at room temperature which revealed the forming of the novel structured material at 1100°C.

Field-emission scanning electron microscopy evidenced the columnar morphology of the particle's agglomeration. High resolution electron transmission microscopy confirms the measured interplanar distances calculated from the XRD. Using the UV-VIS spectra and Kubelka-Munk equations, the absorbance and the band gap for the $Zn_3Nb_2O_8$ nanomaterial were calculated. PL spectra revealed a single peak at 465 nm corresponding to the blue color fluorescence that is preserved also in acrylic based paint and after embedding in isopropyl alcohol.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.



(a) (b)

FIGURE 5: $Zn_3Nb_2O_8$ in (a) acrylic based paint and (b) isopropyl alcohol.

Acknowledgments

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