The aim of this work is firstly to synthesize nanostructures by hydrothermal method. The low temperature hydrothermal synthesis (at 95 °C) is becoming popular for environmental reasons, since water is used as the reaction solvent rather than organics.

Many methods have been used to prepare the ZnO material as one-dimensional (1D) nanostructures with different morphologies including nanowires, nanorods, nanotubes, whiskers, nanocystals, nanobelts and other superstructures [1,2,3]. They represent a large class of nanoscale building blocks that have been used to assemble functional devices such as lasers, photodetectors, field emitters, and transistors, through optical devices, sensors, piezoelectric transducers and actuators, solar cells etc. [3,5-7].

There are several methods to synthesize ZnO nanostructures, such as vapour transport process, chemical bath deposition, sol-gel method, electrochemical deposition, high pressure sodium halides under high pressure, high temperature conditions (Four-Step Method) [1,7].

Low temperature hydrothermal synthesis is a more convenient and economic large scale preparation of self-ordered ZnO nanowires/nanorods arrays compared to VLS, CVD and ED methods, which require sophisticated equipment and rigorous conditions (such as single-crystals substrates) [4].

The aim of this work is firstly to synthesize ZnO nanostructures by hydrothermal method and secondly to investigate the influence of nanowires, nanorods, nanotubes and polyethylene glycol (PEG) and the reaction time at constant temperature on the morphology / dimensions and structure of the final products.

The Raw materials and conditions for the hydrothermal synthesis of ZnO nanostructures are presented in Table 1.

Table 1. Raw materials and conditions for the hydrothermal synthesis of ZnO nanostructures.

<table>
<thead>
<tr>
<th>Code of Materials</th>
<th>Zn(NO₃)₂·6H₂O</th>
<th>Na₂CO₃</th>
<th>PEG</th>
<th>Ethanol</th>
<th>Water</th>
<th>Temperature</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Z-1</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>70</td>
<td>100</td>
<td>95 °C</td>
<td>20</td>
</tr>
<tr>
<td>1Z-2</td>
<td>15</td>
<td>15</td>
<td>10</td>
<td>60</td>
<td>140</td>
<td>95 °C</td>
<td>20</td>
</tr>
<tr>
<td>2Z-1</td>
<td>15</td>
<td>15</td>
<td>10</td>
<td>60</td>
<td>140</td>
<td>95 °C</td>
<td>20</td>
</tr>
<tr>
<td>2Z-2</td>
<td>15</td>
<td>15</td>
<td>10</td>
<td>60</td>
<td>140</td>
<td>95 °C</td>
<td>20</td>
</tr>
</tbody>
</table>

According to literature [5] the growth unit of ZnO crystal is the complex ZnOH₂⁺, the reaction mechanism of ZnO crystals under hydrothermal condition begins with the formation of the growth unit:

\[ Zn^{2+} + 2OH^- = Zn(OH)_2^{2+} \]

and proceeds with the incorporation of growth unit into the newly formed crystal lattice by the oxidation reaction under super saturation condition:

\[ Zn(OH)_2^{2+} + 2OH^- = ZnO(OH)_{2n} + H_2O \]

Finally, when the size of the clusters ZnO(OH)_{2n} reaches the size of the so-called “critical nucleus”, ZnO powders are precipitated.

For the quantification of the unreacted Zn contained in the incubation solution as precipitated from the autoclave after the completion of the reaction, the procedure is as follows: 1 mL of the incubation solution is volumetric measured and 1 mL of this solution is diluted with distilled water to form a diluted solution of 250 mL. From the percentage of unreacted Zn measured with Atomic Absorption Spectroscopy (AAS), the results are presented in Table 2, whereas the amount of Zn in the incubation solution and short growth is calculated by the difference corresponds to the percentage of reacted Zn. The yield of Zn is high fluctuating approximately between 90 and 96 % w/w.

<table>
<thead>
<tr>
<th>Incubant solution of experiments</th>
<th>Volume of incubant solution (mL)</th>
<th>Measured Zn in the incubant solution by AAS (ppm/g/mL)</th>
<th>Percentage of reacted Zn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22-1</td>
<td>100</td>
<td>0.397</td>
<td>95.71</td>
</tr>
<tr>
<td>22-2</td>
<td>100</td>
<td>0.397</td>
<td>95.71</td>
</tr>
<tr>
<td>92-1</td>
<td>110</td>
<td>0.885</td>
<td>90.01</td>
</tr>
</tbody>
</table>

The material obtained from Table 2 shows a good growth behaviour along the axes with morphologies of straight or flowerlike / starlike rods, either ending with regular hexagonal pyramid or starlike structures.

In the material 5Z-2 (Image 7) there are a) single rods, b) many flowerlike or starlike branched structures and c) a soft made of oriented whiskers.

It is characteristic for this material that the rods, branched or not, have ends with regular hexagonal pyramid structure.

All diffraction peaks can be indexed non-crystalline and correspond to the known wurtzite-stressed (hexagonal) ZnO, with lattice constants a and c in agreement with that of literature.

The yield of Zn is high fluctuating approximately between 90 and 96 % w/w.

By increasing the incubant solution of experiments, the amorphous regions are decreased and more rods, branched or not with ends of regular hexagonal pyramid structure are formed and their dimensions are increased (comparison between 1Z-2 and 2Z-1).

By increasing the proportion of PEG, the amorphous regions are further reduced and many flowerlike or starlike branched structures are formed, which have ends with regular hexagonal pyramid structure (comparison between 1Z-1 and 2Z-2).

The use of ethanol without water (4Z-2) leads to very few single rods or branched rods and much amorphous material, therefore water is necessary to be used in the initial solution for the morphological process (comparison between 1Z-2 and 4Z-1).

In the next step, the use of increased amount of water, without ethanol (materials 22-1, 22-2, 22-3, 22-4, 5Z-1 and 5Z-2) leads to the formation of nanocrystalline material without amorphous regions in the forms of single rods or branched, forming flowerlike or starlike ends with regular hexagonal pyramid structure. Under these conditions, ZnO nanostructures are perfectly formed already by one hour, and extended time does not contribute to any increment of the number of nanostructures.

The preparation of this group of materials (second group, materials 22-1, 22-2, 22-3, 5Z-1, 5Z-2, 5Z-3, 5Z-4) with that of the first group (12-1, 12-2, 12-3, 12-4, 12-5, 12-6) it is observed that the percentage of ZnO in these materials is very high, not all products are in crystalline nanostructure form, as is observed in SEM images and in X ray diffraction patterns.

The material 42-1 (Image 6) consists of a) many flowerlike or starlike branched structures and c) a soft made of oriented whiskers.

The material 5Z-2 (Image 7) consists of a) single rods, b) many flowerlike or starlike branched structures and c) a soft made of oriented whiskers.

The material 5Z-1 (Image 8) consists of a) single rods, b) flowerlike or starlike branched structures and c) flowerlike lamellae and c) flowerlike or starlike branched structures.

The above observation is also confirmed by SEM images concluding that material 42-1 has both amorphous regions. The diffractograms of materials 22-1, 22-2, 22-3 and 22-4 show high crystallinity.

The material 42-1 (Image 6) consists of a) single rods, b) flowerlike or starlike branched structures and c) flowerlike lamellae and c) flowerlike or starlike branched structures.

The material 5Z-2 (Image 7) consists of a) single rods, b) flowerlike or starlike branched structures and c) flowerlike lamellae and c) flowerlike or starlike branched structures.

The material 5Z-1 (Image 8) consists of a) single rods, b) flowerlike or starlike branched structures and c) flowerlike lamellae and c) flowerlike or starlike branched structures.

The material 42-1 (Image 6) consists of a) single rods, b) flowerlike or starlike branched structures and c) flowerlike lamellae and c) flowerlike or starlike branched structures.

The material 5Z-2 (Image 7) consists of a) single rods, b) flowerlike or starlike branched structures and c) flowerlike lamellae and c) flowerlike or starlike branched structures.

The material 5Z-1 (Image 8) consists of a) single rods, b) flowerlike or starlike branched structures and c) flowerlike lamellae and c) flowerlike or starlike branched structures.