Bulgarian Chemical Communications, Volume 49 Special Issue G (pp.225 –230) 2017

Synthesis and stability of zinc hydroxide nitrate nanoparticles

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Received October 24, 2016; Revised January 3, 2017

The nanosized zinc hydroxide nitrate has been recently estimated as prospective foliar fertilizer, possessing improved zinc solubility, but low phytotoxicity, in comparison with ZnO and other Zn-containing compounds. The main problem is obtaining stable particles with dimensions less than 100 nm. This work studies the effect of preparation conditions on the chemical compositions and particle size of the zinc hydroxide nitrates prepared by precipitation. $Zn(NO_3)_2{\cdot}6H_2O$ and NaOH were used with concentrations ranging from 0.4 to 3.2 M and the initial OH/Zn ratio of 1.6 at temperatures from 20 to 60°C. All samples were characterized in detail by X-ray diffraction, scanning electron microscopy, thermal analysis, and inductively coupled plasma (ICP). Stability and distribution of the zinc hydroxide nitrate particles were estimated too.

Keywords*:Zinc hydroxide nitrate, nanoparticles, preparation, foliar fertilizer.*

INTRODUCTION

The layered double hydroxides (LDH) family of materials are important compounds with the general formula of $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}]_{x/n}{\cdot}mH_2O$ where M^{II} and M^{III} are di- and trivalent metals, and A^{n-} is an anion (e.g. nitrate) [1]. As modified form of LDH, hydroxide double salts (HDS) with a general formula of $[M^{II}_{1-x}M^{II}_{2x}(OH)_2]^{2x+}[A^{n-}]_{2x/n}{\cdot}mH_2O$ exist, which contain two divalent cations. In case the cations in HDS are the same, the salts are known as "basic salts" [2]. They are precursors for useful materials such as UV absorbents in sunscreen formulations [3] and matrices for immobilization of metal complexes and dyes [4]. Recently, HDS have been intensively studied as potential long-term foliar fertilizers [5, 6]. Zinc hydroxide nitrate ($Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$) seems to be the most promising in this respect. The crystal suspension maintains a Zn^{2+} concentration of 30-50 mg/l which is enough for suffusion leaf uptake without phytotoxicity [7]. Four forms of zinc hydroxide nitrate are known in the scientific literature: $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$, $Zn_5(OH)_8(NO_3)_2$, $Zn_3(OH)_4(NO_3)_2$ and $Zn(OH)(NO_3)_2{\cdot}H_2O$. The last one is not layered [8]. Many efforts are devoted to the preparation of free of impurities nanosized $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$. It is generally accepted that zinc hydroxide nitrate with the ideal composition $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ can be prepared by precipitation from a solution of $Zn(NO_3)_2{\cdot}6H_2O$ with NaOH (OH/Zn ratio 0.5) at room temperature with vigorous stirring. It was found that increasing the OH/Zn ratio, or the reaction temperature, resulted in the formation of ZnO or $Zn(OH)(NO_3)_2{\cdot}H_2O$, in addition to the desired product [7, 8]. The main misadventure of the procedure is the limitation of the OH/Zn ratio, which predicts substantial concentration of Zn^{2+} in the mother liquor. Therefore, the main objective of this research is to develop and optimize the preparation of zinc hydroxide nitrate, $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$, with nanosized dimensions and to evaluate the shelf life of prepared crystals in suspension.

EXPERIMENTAL

Preparation procedure

Materials: Zinc nitrate hexahydrate $Zn(NO_3)_2{\cdot}6H_2O$ and NaOH reagent grade were used in the present experiments.

Synthesis: Preparation of zinc hydroxide nitrate ($Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$) was performed by pouring NaOH solution into $Zn(NO_3)_2{\cdot}6H_2O$ under vigorous stirring. The initial OH/Zn molar ratio was 1.6 (corresponding to stoichiometric OH/Zn molar ratio) and the time of precipitation was 10 minutes in all cases (to prevent transformation of the synthesized zinc hydroxide nitrate to ZnO). Five series of samples (Table 1) were synthesized under the following conditions: a solution containing 120 mmol of NaOH with concentration ranged from 0.4 M to 3.2 M was poured in a solution containing 75 mmol of $Zn(NO_3)_2{\cdot}6H_2O$ with concentration ranged from 0.4 M to 3.2 M under vigorous stirring.

In order to evaluate the influence of the temperature on the parameters of the resulting zinc hydroxide nitrate, more experiments were performed under different conditions, including increasing the temperature to 70 °C and monitoring the precipitate in the mother liquor for one month. The white precipitate was filtered, washed with deionized water and dried at 65°C for 24 h. The scheme of the experiments is presented in Table 1.

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Samples Characterization

Powder X-Ray Diffraction (XRD)

The XRD patterns were recorded on a Philips PW 1050 diffractometer, equipped with Cu Kα tube and a scintillation detector. Data for cell refinements was collected in θ-2θ, step-scan mode in the angle interval from 10 to 90º (2θ) at counting time of 3 s/step and steps of 0.03º (2θ).

Scanning Electron Microscopy (SEM)

SEM images were recorded in a JSM 6390 electron microscope (Japan) in conjunction with energy dispersive X-ray spectroscopy (EDS, Oxford INCA Energy 350) equipped with ultrahigh resolution scanning system (ASID-3D) in a regime of secondary electron image (SEI) and backscattered electrons (BEC). The samples were coated with gold before imaging.

Chemical Analysis

ICP-AES (Prodigy 7, Leeman) was applied to quantify the zinc content in the solid products and filtrates. The pH values were monitored by a pH meter WTW inoLab® pH 7110 (Germany).

RESULTS

The Influence of the main parameters of the synthesis on the chemical composition and morphology of the resulting samples were monitored.

Influence of initial concentration

Chemical Composition

Twenty five samples were prepared according to the scheme presented in Table 1, and zinc content and weight loss (ΔG, %) were determined for each of them. The weight loss was calculated after calcination of the samples for 2 hours at 450°C. The results are presented in Table 2.

The theoretical value of zinc content in the dried at 65°C zinc hydroxide nitrate, calculated for the formula $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, is 52.47%. According to the data of [9] complete decomposition of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ to ZnO ends at 300°C with the weight loss of 34.7%.

A weight loss less than this and zinc content more than 52.47% indicates the presence of impurities with a higher content of zinc (ZnO, $Zn_3(OH)_4(NO_3)_2$ or $Zn(OH)(NO_3) \cdot H_2O$). The results presented in Table 2 correspond very closely to the theoretical ones and suggest the formation of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ in all cases. This suggestion was verified by X-ray and SEM analysis of the fresh samples after filtration and washing with distilled water. Some of these results are shown in Figs. 1-4.

Table 1. Scheme of the experiment

Series	S-1	S-2	S-3	S-4	S-5
$Zn(NO_3)_2.6H_2O$, mol/l	0.4 M	1.2 M	1.6 M	2.4 M	3.2 M
NaOH, mol/l	0.4 M	0.4 M	0.4 M	0.4 M	0.4 M
NaOH, mol/l	1.2 M	1.2 M	1.2 M	1.2 M	1.2 M
NaOH, mol/l	1.6 M	1.6 M	1.6 M	1.6 M	1.6 M
NaOH, mol/l	2.4 M	2.4 M	2.4 M	2.4 M	2.4 M
NaOH, mol/l	3.2 M	3.2 M	3.2 M	3.2 M	3.2 M

Table 2. Chemical composition (Zn, %) and weight loss at 450°C (Δ**G,%**) of the samples synthesized at room temperature

Series	**S-1**	**S-2**	**S-3**	**S-4**	**S-5**
Zn,%	52.3±0.8	51.3±0.9	52.7±0.5	53.1±0.8	52.4±0.6
ΔG,%	34.48	34.57	34.63	34.3	34.8
Zn,%	53.1±0.8	53.4±0.8	51.9±0.8	52.3±0.9	52.7±0.7
ΔG,%	34.53	34.66	34.34	34.85	34.95
Zn,%	52.6±0.8	53.3±0.9	51.9±0.4	52.1±0.6	52.3±0.7
ΔG,%	34.11	34.7	34.87	34.54	34.25
Zn,%	53.3±0.9	51.8±0.8	52.4±0.5	53.1±0.7	53.6±0.8
ΔG,%	34.28	34.02	33.98	34.11	33.73
Zn,%	52.4±0.8	52.9±0.8	52.2±0.7	53.4±0.6	53.8±0.7
ΔG,%	34.46	34.00	34.25	33.60	33.62

Fig. 1 presents the X-ray pattern of the sample synthesized at 25°C and concentration of sodium hydroxide and zinc nitrate 1.6 M. The strongest peak at 2θ = 9.2° and other characteristic peaks at 2θ = 18.4, 34.6, 35.4, 46.8, and 47.4° identified formation of pure well crystallised zinc hydroxide nitrate ($Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, JCPDS card 24-1460).

The results for all other samples were identical except for the last two from series S5. In these cases, a new set of very weak peaks appears at 2θ = 31.8°, 34.5° and 47.4°. These peaks are identical to the JCPDS card 36-1451 for ZnO and indicate the presence of insignificant amounts of zinc oxide and $Zn_3(OH)_4(NO_3)_2$ (2θ = 26.1°, JCPDS card 70-1361). The presence of the last one is not fully clarified (Fig. 2).

Fig. 3 presents the SEM images of the sample synthesized at 25°C and concentration of sodium hydroxide and zinc nitrate 1.6 M. As it can be seen, the sample is composed of sheet-like particles, the typical morphology of zinc hydroxide nitrate. These images are typical for all other samples, prepared according to the scheme presented in Table 1 except for the last two from series S5. The result is consistent with the observation from XRD pattern, presented in Fig. 1 and confirm the obtaining of pure $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$.

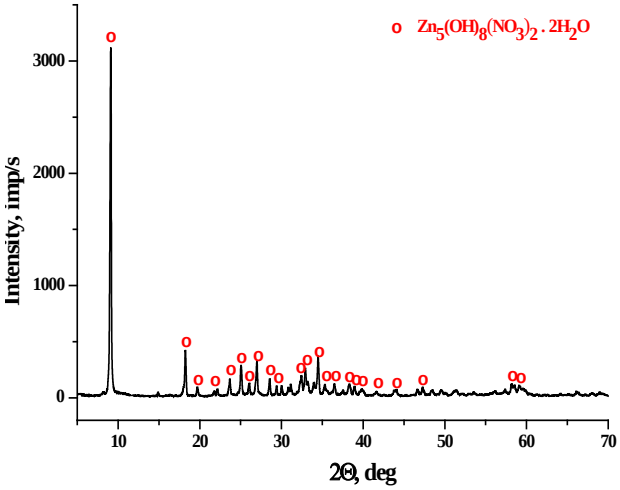


Fig. 1. X-ray pattern of the sample synthesized at 25°C and concentration of NaOH and $Zn(NO_3)_2$ 1.6 M

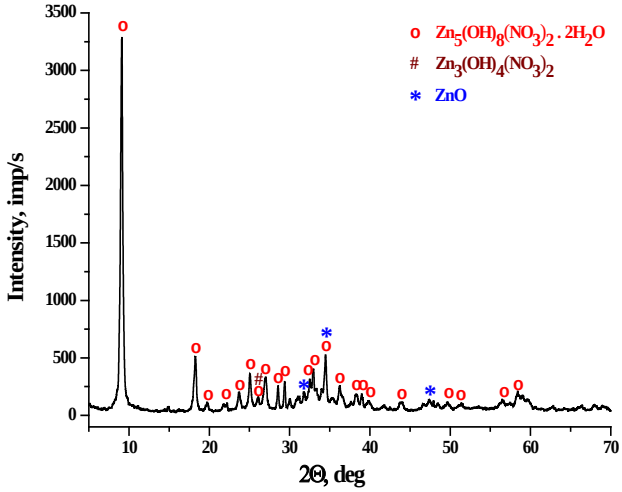
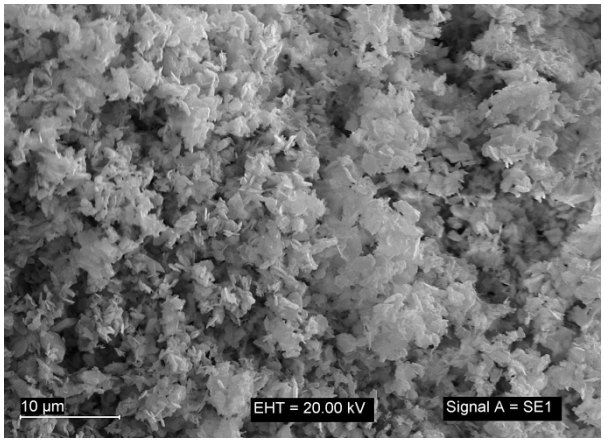
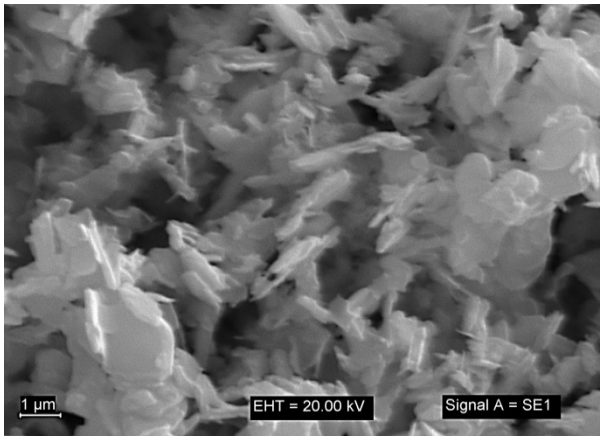


Fig. 2. X-ray pattern of the sample synthesized at 25°C and concentration of NaOH and $Zn(NO_3)_2$ 3.2 M



A



B

Fig. 3. SEM images of samples synthesized at 25°C with initial OH/Zn molar ratio 1.6 and concentration of zinc nitrate and sodium hydroxide 1.6 M. Scale bar: **A:** 10 µm; **B:** 1.0 µm

Fig. 4 presents the SEM images of the sample synthesized at 25°C and concentration of NaOH and $Zn(NO_3)_2$ 3.2 M. The results presented suggest two easily noticeable differences, concerning particle size and sample composition. Fig. 4 (a) demonstrates the same morphology of the resulting precipitate but a visible decrease of the particle size, more often smaller than 1 µm.

A slight morphology change can be seen after careful examination of the image presented in Figs. 4 (b) and (c). Obvious domination of the sheet-like particles with thickness less than 100 nm, belonging to ($Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$) can be seen. Furthermore, although few in number, a new type of particles appears. Probably ZnO crystals or the intermediates to ZnO, as suggested by the weak characteristic peaks of ZnO in the X-ray pattern, presented in Fig. 2.

Influence of temperature and storage time in the mother liquor

Except the concentration of the solutions used in the synthesis, the temperature and acidity of the medium are essential for the composition and stability of the resulting precipitates. Takada [10] investigated the effect of pH on the formation of the zinc compound, including $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$.

A B C

Fig. 4. SEM images of samples synthesized at 25°C with initial OH/Zn molar ratio 1.6 and concentration of zinc nitrate and sodium hydroxide 3.2 M. Scale bar: A: 10 µm; B: 1.0 µm; C: 0.5 µm

In order to accelerate hydrolysis, suspensions containing 0.15 or 0.5 M $Zn(NO_3)_2$ and 1.0 M NaOH with $2OH/Zn^{2+}$ (R) from 0.01 to 2.0 are subjected to ageing on a rotating drum for 100-120 h at 25, 50 and 70ºC. The authors found that a zinc hydroxide nitrate and/or ZnO are formed depending on the $2OH/Zn^{2+}$ value. Impurities of zinc oxide are found at R close to 1.0 and pure ZnO is formed after this point. According to the results presented, increasing the temperature up to 70ºC does not affect the composition of the precipitate obtained.

Similar results are obtained in [7], [11] and [12], which studied in detail the preparation of zinc hydroxide nitrate nanocrystals and their chemical and structural stability. These authors found that this compound can be synthesized by quick precipitation of zinc nitrate and sodium hydroxide solution under various conditions. Transformation in the composition and morphology of the precipitate along the ageing is monitored. It was concluded that zinc hydroxide nitrate crystals are very stable when isolated and then dispersed in aqueous solution.

In our opinion, isolation and drying of the precipitate is not the best approach for the successful preparation of foliar fertilizer. The main reason is the sintering of the partials, leading to a rapid decrease in its affectivity. This is why the shelf life of the precipitate in the mother liquor after synthesis is extremely important in terms of the use of the basic zinc nitrate as foliar fertilizer. Therefore, we changed the method of investigating the stability of the synthesized samples by limiting the time of synthesis to 10 minutes. The precipitates obtained at higher temperatures were cooled rapidly to room temperature and ongoing processes in the thus obtained suspensions were monitored for 30 days.

Figs. 5 and 6 show the temperature influence on the samples prepared at 70ºC, initial OH/Zn molar ratio 1.6 and concentration of the NaOH and $Zn(NO_3)_2$ 3.2 M.

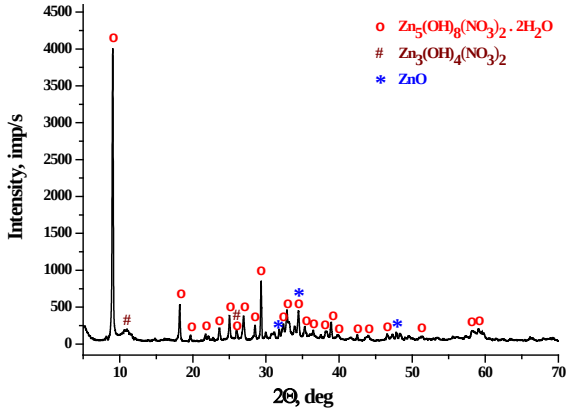
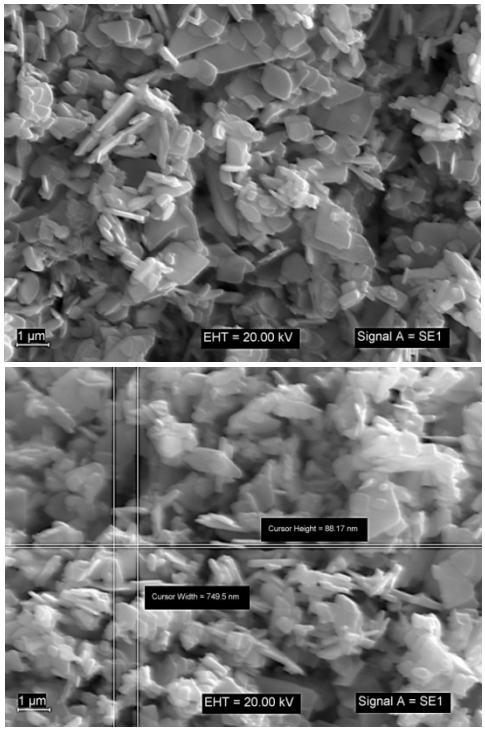


Fig. 5. XRD patterns of sample prepared at 70ºC, initial OH/Zn molar ratio 3.2 and concentration of the zinc nitrate and sodium hydroxide 3.2 M



A B

Fig. 6. SEM images of sample synthesized 70ºC, initial OH/Zn molar ratio 3.2 and concentration of the zinc nitrate and sodium hydroxide 3.2 M. Scale bar: A: 1.0 µm; B: 1.0 µm.

No substantial change in the composition and morphology of the resulted sample can be observed. The sheet-like particles of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ dominate and traces of $Zn_3(OH)_4(NO_3)_2$ are also present. This result confirms the suggestion that increasing the temperature to 70°C slightly affects the crystal phase and morphology of the precipitate. The shelf life in the mother liquor of the precipitate obtained at 25 and 75°C was monitored. The results are presented in Tables 3 and 4.

The results presented in Tables 3 and 4 correspond very closely to the theoretical ones and suggest no change in the composition and morphology of the precipitate. This suggestion was confirmed by the results of X-ray and SEM analysis, which are similar to the results presented above. Obviously the crystal phase does not undergo detectable change along the storage in the mother liquor (up to 30 days).

Table 3. Chemical composition (Zn, %) and weight loss at 450°C (**ΔG,%**) of the samples synthesized at room temperature, OH/Zn molar ratio 1.6 and NaOH and $Zn(NO_3)_2$ concentration 1.6 M after 30 days storage in mother liquor

№	Time	Zn, %	ΔG, %	pH
1	Immediately	53.4 ± 0.8	34.61	5.98
2	1 hour	52.0 ± 1.0	34.12	6.01
3	3 hours	53.1 ± 0.9	34.00	6.01
4	5 hours	52.6 ± 0.7	33.84	6.00
5	8 hours	53.2 ± 0.8	34.65	6.00
6	1 day	51.2 ± 0.9	34.13	6.00
7	10 days	52.0 ± 0.6	35.12	6.02
8	20 days	51.3 ± 1.0	34.53	6.03
9	30 days	53.2 ± 0.8	33.91	6.06

Table 4. Chemical composition of the samples synthesized at 70°C, OH/Zn molar ratio 1.6 and NaOH and $Zn(NO_3)_2$ concentration 3.2 M after 30 days storage in mother liquor at room temperature

№	Time	Zn, %	ΔG, %	pH
1	immediately	52.0 ± 0.8	34.22	6.10
2	1 hour	52.8 ± 1.0	34.81	6.15
3	3 hours	53.1 ± 0.8	33.52	6.14
4	5 hours	52.9 ± 0.8	33.81	6.18
5	8 hours	52.2 ± 0.8	34.90	6.18
6	1 day	53.2 ± 0.9	34.10	6.17
7	10 days	53.0 ± 1.0	35.11	6.15
8	20 days	53.1 ± 0.9	34.53	6.10
9	30 days	52.8 ± 0.8	35.62	6.10

The essential difference between the results obtained by us and those of other authors can be explained with the very low speed of hydrolysis processes at room temperature, leading to the transformation of the $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ to ZnO. The minor change in pH values is noteworthy, which also confirms the absence of significant processes in the frame of the investigated time period.

CONCLUSIONS

Zinc hydroxide nitrate has been synthesized by precipitation of zinc nitrate in sodium hydroxide solution under various conditions. The phase transformation from zinc hydroxide nitrate to ZnO or other intermediate compounds has been examined. A long-term stability of the crystal phase in the mother liquor was found which identifies the zinc hydroxide nitrate suspension as a promising feedstock for the preparation of foliar fertilizer.

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СИНТЕЗ И СТАБИЛНОСТ НА НАНОКРИСТАЛИ ОТ ЦИНКОВ ХИДРОКСИНИТРАТ

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Постъпила на 24 октомври 2016 г.; приета на 3 януари 2017 г.

(Резюме)

Наноразмерният цинков хидрокси нитрат се оценява като перспективен листен тор с по-добра разтворимост от ZnO и с по-ниска фитотоксичност в сравнение с други цинк-съдържащи съединения. Основният проблем е получаването на стабилни кристали с размери под 100 nm. Това изследване има за цел да оцени влиянието на условията на получаване върху химическия състав и големината на частиците на цинковия хидрокси нитрат, синтезиран чрез съутаяване на $Zn(NO_3)_2 \cdot 6H_2O$ и NaOH с концентрация на изходните разтвори от 0.4 до 3.2 M и молно отношение OH/Zn 1.6 при температури на синтез от 20 до 60°C. Всички образци са детайлно охарактеризирани чрез рентгеноструктурен анализ, сканираща електронна микроскопия, термичен и елементен (ICP) анализ. Изследвана е също стабилността на кристалите от цинков хидрокси нитрат при престой в маточния разтвор до 30 дни.

Ключови думи: *цинков хидрокси нитрат, наночастици, синтез, листен тор.*