*Journal of Chemical Technology and Metallurgy, 58, 1, 2023, 14-32*

# SYNTHESIS OF LAYERED COPPER-ZINC HYDROXIDE NITRATE NANOPARTICLES: NEW APPROACH, NEW INSIGHTS

Krasimir Ivanov[1], Elitsa Kolentsova[1], Dimitar Dimitrov[1], Daniela Karashanova[2],
Nguyen Cao Nguyen[1]

[1]*Department of Chemistry, Agricultural University – Plovdiv*
*12 Mendeleev blvd., 4000 Plovdiv, Bulgaria*
[2]*Institute of Optical Materials and Technologies*
*Acad. G. Bonchev str., bl.109, 1113 Sofia, Bulgaria*
*E-mail: kivanov1@abv.bg*

*Received 04 April 2022*
*Accepted 27 May 2022*

## ABSTRACT

*This study is aimed to the development of knowledge about the preparation, properties and thermal decomposition of mixed Zn-Cu nanosized hydroxy nitrates. It will help to expand their use as precursors to produce important for practice nanostructured materials. The precipitation of the mixed hydroxy nitrates was carried out at 60°C by (i) pouring 3.6 M KOH into nitrate mixture and (ii) by dropwise adding copper nitrate and sodium hydroxide simultaneously to the zinc nitrate solution. Pure* $Zn_5(OH)_8(NO_3)_2\times 2H_2O$, $Zn_3(OH)_4(NO_3)_2$ *and* $Cu_2(OH)_3NO_3$ *as reference compounds were synthesized as well as five mixed Cu-Zn hydroxide nitrate with composition* $Cu_{20}Zn_{80}$, $Cu_{40}Zn_{60}$, $Cu_{50}Zn_{50}$, $Cu_{60}Zn_{40}$ *and* $Cu_{80}Zn_{20}$. *XRD, FTIR, SEM, TEM, ICP-AES and thermal analysis were used for samples' characterization. It is established that in all cases of copper nitrate and zinc nitrate coprecipitation, the host material in the mixed samples is* $Cu_2(OH)_3(NO_3)_2$. *On the opposite, in the case of mixed Zn-Cu oxides, prepared by thermal decomposition of mixed Cu-Zn hydroxy nitrates the host material is ZnO. The composition of the mixed Cu-Zn hydroxy nitrates strongly depends on the molar ratio Cu/Zn in the stock solution. At a molar ratio Cu/Zn < 1.0 the synthesized samples contain* $Zn_5(OH)_8(NO_3)_2\times 2H_2O$ *and* $(Zn_1Cu_1)(OH)_3NO_3$, *and at a molar ratio Cu/Zn > 1.0 -* $Cu_2(OH)_3NO_3$ *and* $(Zn_1Cu_1)(OH)_3NO_3$.

*Keywords: layered hydroxy nitrates, copper-zinc hydroxide nitrate, copper-zinc oxides, nanoparticles.*

## INTRODUCTION

The layered double hydroxides (LDH) are an important family of compounds with the general formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot mH_2O$ where $M^{2+}$ and $M^{3+}$ are di- and trivalent metals, and $A^{n-}$ is an anion (e.g. nitrate) [1, 2]. The hydroxide double salts (HDS) are modified form of LDH with the general formula $[M^{2+}_{1-x}M^{2+}_{2x}(OH)_2]^{2x+}[A^{n-}]_{2x/n}\cdot mH_2O$, which contain two divalent cations. In case the cations in HDS are the same, the salts are known as layered hydroxy salts (LHS) or "basic salts" [3]. They can be separated into two structural types, based on the structure of zinc hydroxy nitrate ($Zn_5(OH)_8(NO_3)_2.2H_2O$) or copper hydroxy nitrate ($Cu_2(OH)_3NO_3.H_2O$) [4, 5]. The thermal decomposition of LHS at moderate temperatures leads to the formation of monocrystalline single and mixed oxides, which are of particular interest to the practice [6]. Copper hydroxy salts have been widely used to prepare $Cu(OH)_2$ and CuO nanocrystals with new morphologies [7].

During the past decade, mixed metal oxide semiconductors have gained great attention from researchers from various fields such as physics, chemistry, and material science due to their various practical applications such as photocatalyst, sensor, microelectronic circuit fabrication, piezoelectric devices, fuel cell, and solar cell [8 - 11]. In this context, researchers have shown great interest to ZnO and the possibilities to enhance its properties by modifying with other elements. Copper oxide-zinc oxide (CuO-ZnO) mixed semiconductors recently are the object of special attention [12 - 15]. Many methods have been used to produce doped zinc oxide materials such as sol-gel, co-precipitation, chemical vapor deposition, etc. However, the use of zinc and copper layered materials as precursors to produce doped zinc oxide are singular [16, 17]. Filling this knowledge gap requires a thorough investigation of the preparation, properties and thermal decomposition of this group of compounds.

The potential of LHS for successful application in many areas of the chemical industry and agriculture is also not sufficiently appreciated. Pure or modified Zn-Cu oxides deposited on different carriers are used as catalysts for various chemical processes [18], primarily for the synthesis of methanol [19, 20]. Their catalytic activity, morphology and phase composition depend essentially on the properties of the precursor and the mechanism of its decomposition. As the precursors are commonly used Cu-Zn hydroxide carbonates or hydroxide nitrates [21, 22]. In our previous study, a series of mixed Cu (II) - Zn (II) hydroxide nitrate crystals of the general formula $Zn_xCu_{2-x}(OH)_3NO_3$ ($0 < x \leq 1.8$) were successfully synthesized by co-precipitation from diluted nitrate solutions with NaOH [23]. Their decomposition results in an oversaturated solid solution of Cu in ZnO, followed by its stratification to CuO and a stable solid solution with a lower Cu content.

An important area of research in layered hydroxy salts is related to the development of a new generation of leaf fertilizers containing nanosized crystals of an individual or mixed zinc and copper hydroxy nitrates [24 - 27]. Furthermore, antibacterial properties are observed for the material [28].

The layered hydroxy nitrates can be produced very simply by using cheap chemicals. This extends the possibility to use them as suitable precursors for obtaining large scale nanocrystals with controlled composition. Typically, the layered hydroxy salts are obtained by co-precipitation of the corresponding nitrates in an alkaline medium at vigorous stirring and temperature up to 100$^o$C, filtration, washing and drying at 50 - 65$^o$C. Since the solubility of $Cu_2(OH)_3NO_3$ ($K_{sp} = 4.2x10^{-17}$) is much lower than that of $Zn_5(OH)_8(NO_3)_2{\times}2H_2O$ ($K_{sp} = 2.5x10^{-14}$) usually copper-zinc nitrate and base are added simultaneously to the zinc nitrate solution [16, 23, 25]. The concentration of solutions, OH/(Zn + Cu) and Zn/Cu molar ratio, temperature and reaction time vary widely. Li et al. used solutions with a low concentration of reagents (0.2 M) and OH/(Zn + Cu) ratio equal to 0.5 at 50°C, as the base and copper nitrate, are simultaneously added into the solution of $Zn(NO_3)_2$ [25]. The same approach was used by Markov et al. at 100$^o$C and Zn/Cu molar ratio within the range $9.1 < Cu/Zn > 1/9$ [23]. Ghotbi et al. are synthesized copper doped nanostructured zinc oxides by using a series of copper doped zinc hydroxide nitrates, prepared by pouring $Cu(NO_3)_2$ and NaOH into $Zn(NO_3)_2$ at constant pH 7.0 ± 0.05 [16]. Thaweesaeng et al. reported the preparation of Cu-doped ZnO nanopowders with up to 5 wt. % Cu by co-precipitation of concentrated (5 M) zinc nitrate ($Zn(NO_3)_2.6H_2O$) and proper amount of copper(II) nitrate ($Cu(NO_3)_2{\times}3H_2O$) at final pH = 14 [17].

The study aims to gain new knowledge about the preparation, properties and thermal decomposition of mixed Zn-Cu nanosized hydroxy nitrates. This will help to expand their use as precursors to produce important for practice nanostructured materials.

## EXPERIMENTAL

As noted above, the mixed layered hydroxy salts are most often prepared by co-precipitation of dilute solutions of the corresponding nitrates in an alkaline medium. More often copper nitrate and NaOH are added simultaneously dropwise to the zinc nitrate solution. In our study, we chose a new approach using a mixture of concentrated solutions of zinc and copper nitrates (3.6 M) and an initial OH/Zn molar ratio OH/(Zn+Cu) = 1.6. In all experiments the time of precipitation was 10 min. The precipitation of the mixed hydroxy nitrates was carried out at 60°C by (i) pouring 3.6 M KOH into nitrate mixture and (ii) by dropwise adding copper nitrate and KOH simultaneously to the zinc nitrate solution. After filtration and washing with distilled water, the resulting precipitate was dried at 65$^o$C for 12 h. All chemicals used are reagent grade (Merk AG). The results for the mixed Cu-Zn hydroxy nitrates were very similar, so herein only those obtained by the second method will presented.

Zinc hydroxy nitrate with the composition $Zn_5(OH)_8(NO_3)_2{\times}2H_2O$ was synthesized by the precipitation method. KOH solution was poured into $Zn(NO_3)_2{\times}6H_2O$ solution under vigorous stirring at 60$^o$C for 10 min. The initial OH/Zn molar ratio was 1.6 and the concentration of all compounds was 1.6 M. Copper hydroxy nitrate with composition $Cu_2(OH)_3NO_3$ was synthesized by precipitation from a 3.2 M $Cu(NO_3)_2{\times}3H_2O$ at OH/Cu molar ratio of 1.5. The hydroxy nitrate with composition $Zn_3(OH)_4(NO_3)_2$

was obtained as described by Chouillet et al. (heating of $Zn(NO_3)_2 \times 6H_2O$ at 120°C for 7 days) [29].

The XRD patterns were recorded on a Philips PW 1050 diffractometer, equipped with Cu Kα tube and a scintillation detector. Data for cell refinements were collected in θ-2θ, a step-scan mode in the angle interval from 10 to 90° (2θ) at a counting time of 3 s/step and steps of 0.03° (2θ). Chemical bonding information on hydroxyl, metal-oxygen and intercalated nitrate group was investigated with Fourier transform infrared spectroscopy (FTIR, BRUKER Vortex 70 spectrophotometer in the range 400 - 4000 $cm^{-1}$) using KBr pellet technique. 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. Computerized thermal installation "Stanton Redcroft" (England) was used for thermal analysis of the samples under the following experimental conditions: heating temperature range 20 - 450°C, Simultaneous analysis of the evolved gases were performed via mass spectrometry using an OmniStar mass spectrometer connected to the TG apparatus. ICP-AES (Prodigy 7, Leeman) was applied to quantify the zinc content in the solid products after digestion. The pH was monitored by pH meter WTW inoLab® pH 7110 (Germany).

## RESULTS AND DISCUSSION

The following copper and zinc hydroxide nitrates have been reported: $Cu_2(OH)_3NO_3$, $Cu_2(OH)_3NO_3.H_2O$, $Zn_5(OH)_8(NO_3)_2.2H_2O$, $Zn_3(OH)_4(NO_3)_2$, $Zn_2(OH)_2(NO_3)_2.2H_2O$ and $Zn(OH)NO_3$ (the latter not having layered structure). However, only $Zn_5(OH)_8(NO_3)_2 \times 2H_2O$ ($Zn_5HN$) precipitates when the zinc nitrate solution is added to the base. Alkalisation of an aqueous solution of copper nitrate results in $Cu_2(OH)_3NO_3$ ($Cu_2HN$). The $Cu_2HN$ and $Zn_3(OH)_4(NO_3)_2$ belong to the so-called "single-layered type" hydroxy salts [4]. Their structure is derived from that of brucite ($Mg(OH)_2$) and in this point of view, both compounds can be considered isostructural. That suggests possibilities for isomorphous substitution of the metal ions. Moreover, the ionic radius of $Cu^{2+}$ = 73 pm and this of $Zn^{2+}$ = 74 pm. Thus the difference in the radii is less than 0.3 nm and favor a substitution. A major problem with the preparation of mixed hydroxy nitrates of copper and zinc is the significant difference in the solubility of $Zn_5HN$ and $Cu_2HN$ ($K_{sp} = 2.5x10^{-14}$ and $K_{sp} = 4.2x10^{-17}$, respectively). This requires careful selection of synthesis conditions (temperature, the concentration of solutions and their mixing).

For the study, $Zn_5(OH)_8(NO_3)_2 \times 2H_2O$, $Zn_3(OH)_4(NO_3)_2$ and $Cu_2(OH)_3NO_3$ as reference compounds were synthesized. The resulting information on the composition, structure and properties of the pure compounds was used in the interpretation of the results for the composition, structure and properties of mixed hydroxy nitrates.

### Preparation and characterization of reference hydroxy nitrates

The theoretical value of zinc content in the dried at 65°C zinc hydroxide nitrate, calculated based on the formula $Zn_5(OH)_8(NO_3)_2 \times 2H_2O$ is 52.47 %. According to the data of Moezzi et al. complete decomposition of $Zn_5HN$ ends at 300°C with a weight loss of 34.67 % [30]. For $Zn_3(OH)_4(NO_3)_2 \times 2H_2O$ these values are 50.54 % and 37.09 % [31] and for $Cu_2(OH)_3NO_3$ - 52.93 % Cu and weight loss of 33.81 % [32]. Zinc and Cu content more than calculated and weight loss less than theoretical indicates the presence of impurities (most probably ZnO or CuO).

The data presented in Table 1 show that the results of weight loss and Cu and Zn content in the synthesized samples are very close to the theoretical ones. This leads us to assume that the compounds thus obtained are pure and free from impurities.

However, to be used as reference materials, information on their crystal structure, morphology, and thermal decomposition is also required. This information is presented in Figs. 1 - 4. Fig. 1 presents the phase compositions of powder samples before and after calcination.

The first pattern is identified as zinc hydroxide nitrate with composition $Zn_5(OH)_8(NO_3)_2.2H_2O$ (JCPDS card 72-0627). The strongest peak at 2θ = 9.2° and other characteristic peaks at 2θ = 18.4, 34.6, 35.4, 46.8, and 47.4° confirm the formation of pure well-crystallized compound. XRD patterns with the strongest peak at 2θ = 15.1 and characteristic peaks at 2θ = 21.5, 25.75 and 33.6

Table 1. Weight loss and Cu and Zn content of the synthesized samples.

| Sample | ΔG, %* |  | Cu, wt. %** | Zn, wt. %** |
|---|---|---|---|---|
|  | Calculated | Observed |  |  |
| $Cu_2(OH)_3NO_3$ | 33.81 | 33.45 | 53.60 ± 1.22 | - |
| $Zn_5(OH)_8(NO_3)_2{\times}2H_2O$ | 34.67 | 33.40 | - | 52.53 ± 1.34 |
| $Zn_3(OH)_4(NO_3)_2{\times}2H_2O$ | 37.09 | 36.44 | - | 50.43 ± 1.28 |

*ΔG* – Weight loss on heating the samples at 400 ° C.*
***Data represent mean of tree independent replicates ± standard deviation.*

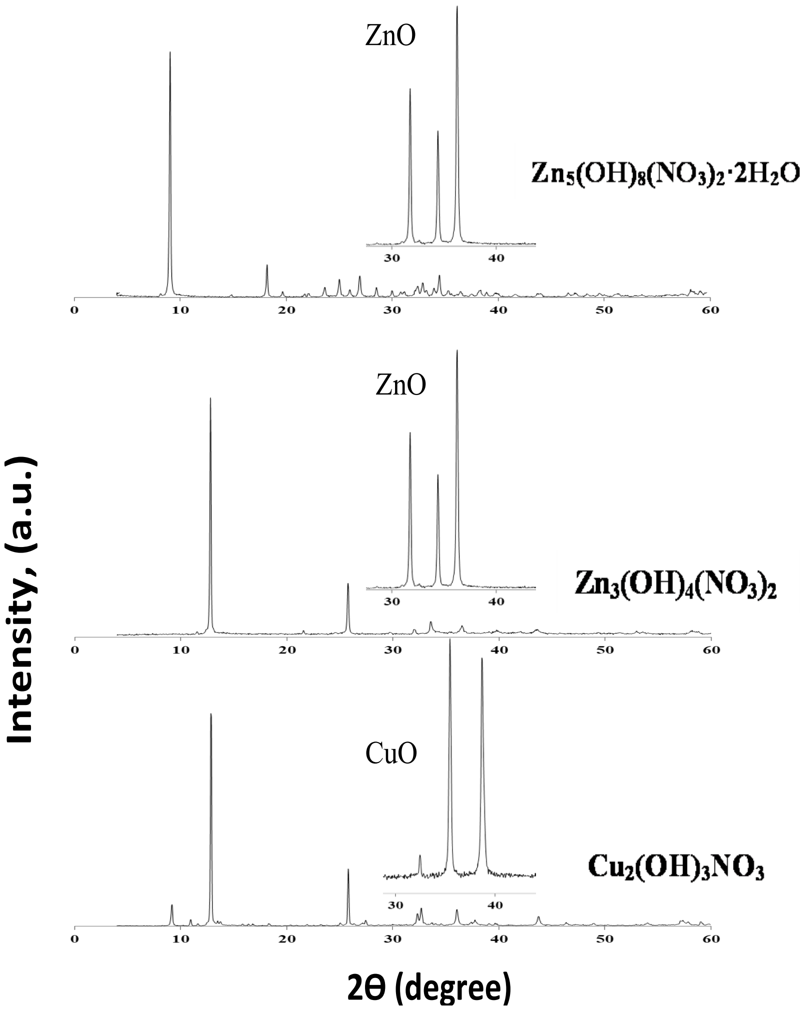


Fig. 1. XRD patterns of $Zn_5(OH)_8(NO_3)_2.2H_2O$, $Zn_3(OH)_4(NO_3)_2$, $Cu_2(OH)_3NO_3$, ZnO and CuO.

and XRD patterns with the strongest peak at 2θ = 12.85 and characteristic peaks at 2θ = 25.8, 32.65, 36.0 and 43.8 fit very well to the literature data for $Cu_2(OH)_3NO_3$ (JCPDS card 15-0014) and $Zn_3(OH)_4(NO_3)_2$ (JCPDS card 70-1361). The diffractograms of pure zinc oxide and copper oxide with characteristic peaks at 2θ = 31.75. 34.4, 36.25$^o$ and 32.45, 35.45, 38.65$^o$ respectively, are added. No major characteristic peaks of the oxides can be found in the spectra of pure hydroxy nitrates, confirming their pure appearance.

FT-IR spectra of as-prepared pure hydroxy nitrates were performed to identify the functional groups (Fig. 2.).

In the $Cu_2HN$ spectrum (Fig. 2A), the sharp peak at 3545 cm$^{-1}$ and the wideband at 3430 cm$^{-1}$ belong to the hydroxyl group, associated with $Cu^{2+}$ and $NO_3^-$. The intensive peaks around 1340 cm$^{-1}$ and 1420 cm$^{-1}$ and the weak peaks around 720 cm$^{-1}$, 810 cm$^{-1}$ and 1045 cm$^{-1}$ characterize various vibration modes of the nitrate group [33]. The bands at 879 cm$^{-1}$, 783 cm$^{-1}$, and 678 cm$^{-1}$ are due to the bending vibrations of Cu–OH groups with different hydrogen bonds [33]. The absence of the peaks at 3300 cm$^{-1}$ and around 1640 cm$^{-1}$ in the $Cu_2HN$ spectrum confirms that $Cu_2HN$ crystals contain no crystalline water molecules.

The FT-IR spectrum (Fig. 2B) confirms the different structure information for the compounds. Various stretching vibrations of O–H bonds in $Zn_5HN$ spectrum lead to a sharp absorption at 3576 cm$^{-1}$, a strong band at 3486 cm$^{-1}$ and a shoulder at 3300 cm$^{-1}$. The shoulder around 3300 cm$^{-1}$ and the peak at 1638 cm$^{-1}$ indicate the presence of water molecules located in the interlayer space or adsorbed water on the surface [34]. The intensive peak around 1380 cm$^{-1}$ and the weak peak at 840 cm$^{-1}$ characterize the various vibration modes of the nitrate group. The characteristic peak at 1507 cm$^{-1}$ can be associated with OH banding mode of the layer hydroxyls [35].

The spectrum of $Zn_3HN$ (Fig. 2C) is characterized

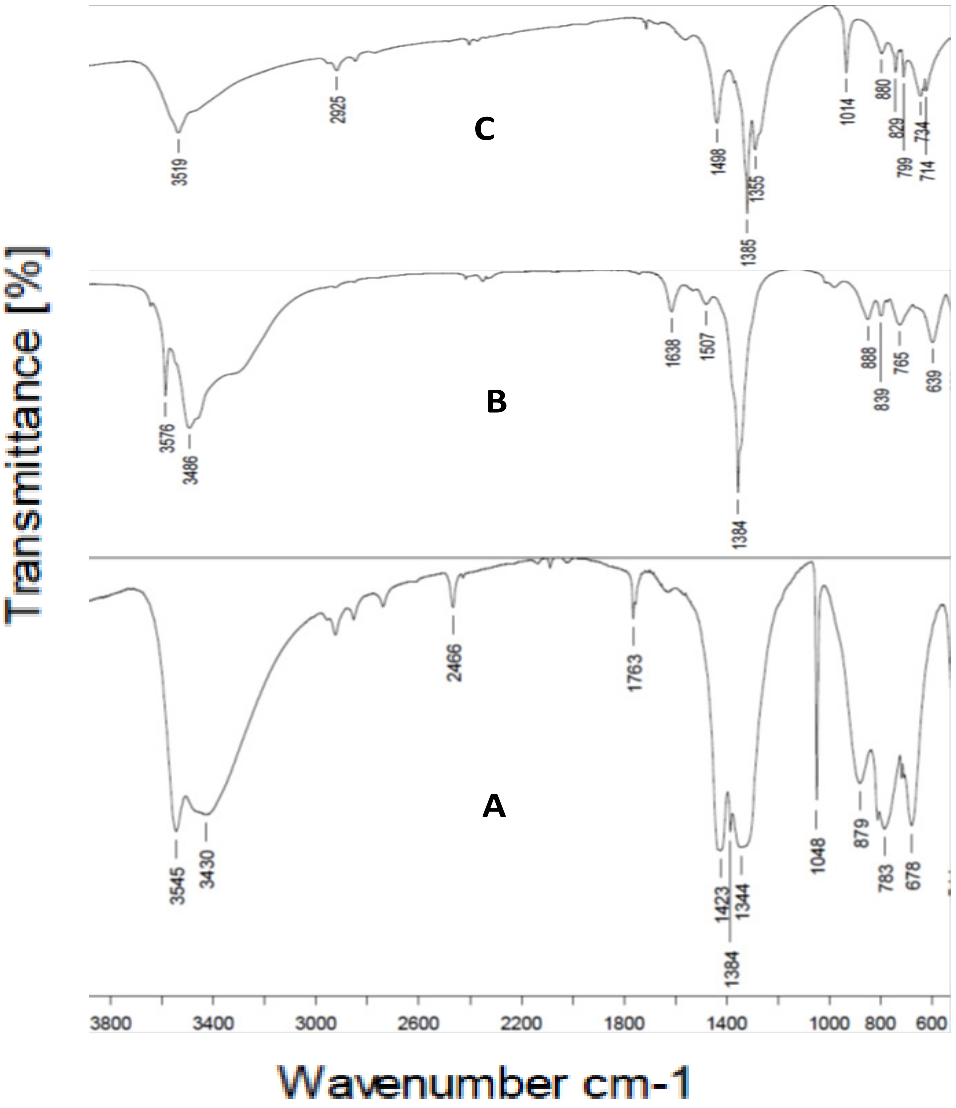


Fig. 2. FT-IR spectra of $(Cu_2(OH)_3NO_3$ (A), $Zn_5(OH)_8(NO_3)_2.2H_2O$ (B), and $Zn_3(OH)_4(NO_3)_2$ (C) samples.

by absorption bands centered at 1385 $cm^{-1}$ and 829 $cm^{-1}$ indicating the presence of nitrate ions. The OH vibration mode gives a broad peak at 3519 $cm^{-1}$. The attribution of the sharp peak at 1014 $cm^{-1}$ is not straightforward. It may be due either to an OH bending mode as for $Zn_5HN$, or to the NO stretching band expected between 1034 $cm^{-1}$ and 970 $cm^{-1}$ for a unidentate coordinated nitrate.

Results of differential thermal analysis (DTA), differential thermal gravimetry (DTG), and thermal gravimetry (TG) analysis of $Zn_5(OH)_8(NO_3)_2{\times}2H_2O$, $Zn_3(OH)_4(NO_3)_2$ and $Cu_2(OH)_3NO_3$ are presented in Fig. 3. Analysis for $H_2O$, NO and $NO_2$ is given only for $Cu_2(OH)_3NO_3$.

From the results presented, it can be seen that the thermal decomposition of the three compounds proceeds in a fundamentally different way, in all cases the end product is the corresponding oxide. It makes the results obtained very useful in clarifying the composition and structure of mixed hydroxy nitrates.

The thermal decomposition of $Zn_5HN$ is a four-step process (Table 2) occurring in the temperature range of 75°C to 300°C. There is no consensus in the scientific literature about its mechanism, but it is generally accepted that the first stage is related to the loss of 2 molecules of water ($\Delta G = 6.1$ %), the second - to the decomposition of $Zn_5HN$ to $Zn_3HN$ ($\Delta G = 5.8$ %) and the last two - with the decomposition of $Zn_3HN$ to ZnO ($\Delta G = 21.5$ %). $Zn_3HN$ undergoes decomposition in two stages and $\Delta G = 17.2$ and 19.2 % respectively, and the decomposition of CuHN occurs at a single step with $\Delta G = 33.4$. TG/DTA curves are in full agreement with the results obtained by the XRD, FTIR and SEM analysis.

Fig. 4. shows the SEM images of $Zn_5(OH)_8(NO_3)_2.2H_2O$ (A), $Zn_3(OH)_4(NO_3)_2$ (B), $Cu_2(OH)_3NO_3$ (C) samples.

SEM images show that the synthesized hydroxy nitrates have a very different morphology. Only uniform sheet-like particles with a thickness less than 100 nm, typical for zinc hydroxide nitrate with composition $Zn_5(OH)_8(NO_3)_2.2H_2O$, can be seen in the first image. $Zn_3HN$ (B) crystallizes in the form of well-formed

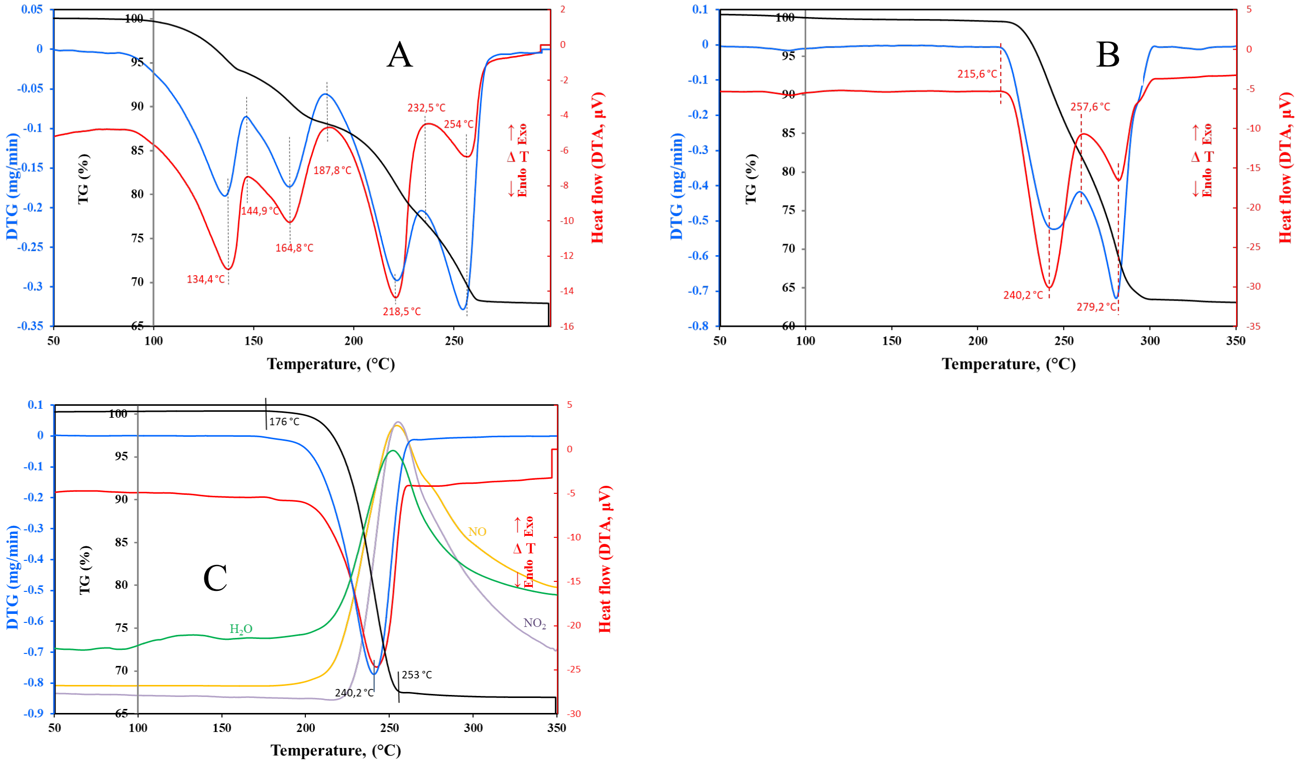
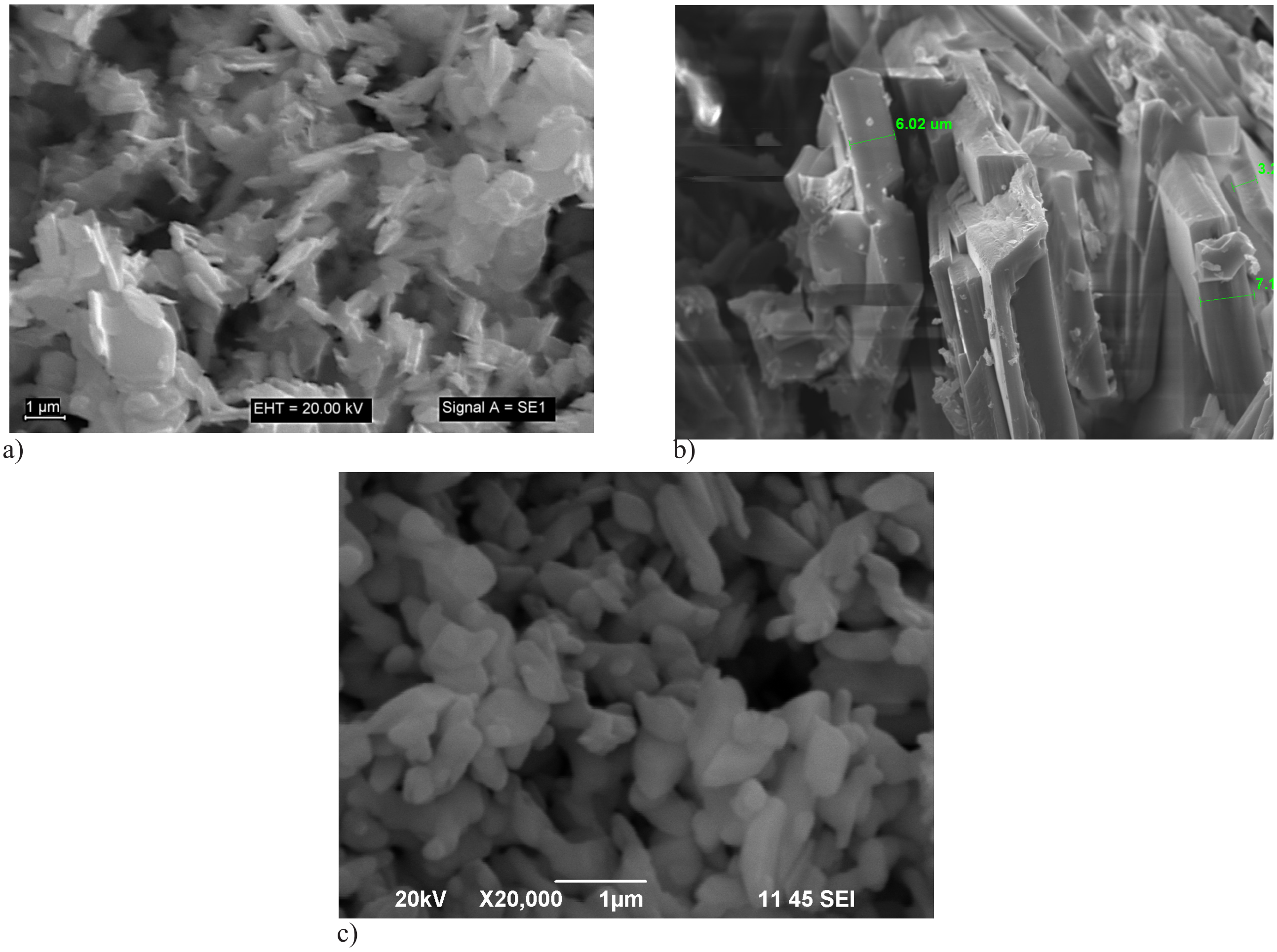


Fig. 3. Simultaneous DTA, DTG, and TG curves of $Zn_5(OH)_8(NO_3)_2.2H_2O$ (A), $Zn_3(OH)_4(NO_3)_2$ (B) and $Cu_2(OH)_3NO_3$ (C).

Table 2. TG data of $Zn_5HN$, $Zn_3HN$ and $Cu_2HN$.

| Sample | Weight loss | | | |
|---|---|---|---|---|
| | First | Second | Third | Forth |
| | (Weight loss)<br>Onset temp.,°C<br>(Edge temp., °C) | (Weight loss)<br>Onset temp.,°C<br>(Edge temp., °C) | (Weight loss)<br>Onset temp.,°C<br>(Edge temp., °C) | (Weight loss)<br>Onset temp.,°C<br>(Edge temp., °C) |
| $Zn_5HN$ | (6.1) 83 (136) | (5.8) 145 (165) | (10.8) 188 (219) | (10.7) 233 (254) |
| $Zn_3HN$ | (17.2) 216 (240) | (19.2) 258 (279) | - | - |
| CuHN | (33.4) 176 (240) | - | - | - |



a)

b)

c)

Fig. 4. SEM images of $Zn_5(OH)_8(NO_3)_2.2H_2O$ (A), $Zn_3(OH)_4(NO_3)_2$ (B), $Cu_2(OH)_3NO_3$ (C) samples.

square-shaped plates between 2 µm and 10 µm. The shape of $Cu_2(OH)_3NO_3$ (C) is characterized by belt-like particles, having a size of less than 1.0 µm. All results presented are in agreement with the literature data and confirm the obtaining of pure $Zn_5(OH)_8(NO_3)_2.2H_2O$, $Zn_3(OH)_4(NO_3)_2$ and $Cu_2(OH)_3NO_3$.

## Preparation and characterization of mixed copper-zinc hydroxy nitrates

Five mixed Cu-Zn hydroxy nitrates covering the entire concentration range of 20 % to 80 % Cu were synthesized: $Cu_{20}Zn_{80}$, $Cu_{40}Zn_{60}$, $Cu_{50}Zn_{50}$, $Cu_{60}Zn_{40}$ and $Cu_{80}Zn_{20}$ (Table 3). The table presents calculated and

Table 3. Composition of $Cu_{20}Zn_{80}$, $Cu_{40}Zn_{60}$, $Cu_{50}Zn_{50}$, $Cu_{60}Zn_{40}$ and $Cu_{80}Zn_{20}$ samples.

| Sample | Cu/Zn molar ratio | | ΔG, %* | Cu, wt. % | Zn, wt. %** |
|---|---|---|---|---|---|
| | Calculated | Observed | | | |
| $Cu_{20}Zn_{80}$ | 20/80 | 21.5/78.5 | 33.84 ± 1.02 | 11.21 ± 0.28 | 42.22 ± 1.22 |
| $Cu_{40}Zn_{60}$ | 40/60 | 40.9/59.1 | 33.47 ± 0.96 | 20.02 ± 0.46 | 29.81 ± 1.46 |
| $Cu_{50}Zn_{50}$ | 50/50 | 49.9/50.1 | 33. 48 ± 0.86 | 25.10 ± 0.48 | 25.00 ± 0.48 |
| $Cu_{60}Zn_{40}$ | 60/40 | 61.6/38.4 | 33.48 ± 0.88 | 33.12 ± 1.15 | 21.23 ± 1.12 |
| $Cu_{80}Zn_{20}$ | 80/20 | 81.0/19.0 | 33.67 ± 1.00 | 43.21 ± 1.28 | 10.44 ± 1.00 |

**ΔG – Weight loss after calcination at 400 °C. **Data represent the mean of three independent replicates ± standard deviation.*

found Cu/Zn molar ratio, weight loss after calcination at 400°C (ΔG) and Cu and Zn content in dried at 65°C samples.

The results presented in Table 3 confirm that the precipitation of the mixed hydroxy nitrates is complete and the content of Cu and Zn in them is very close to the theoretical calculation. The ΔG values for all samples are between the values of the pure compounds $Zn_5(OH)_8(NO_3)_2×2H_2O$ (34.67) and $Cu_2(OH)_3NO_3$ (33.4). This suggests that mixed hydroxy nitrates contain only these compounds in pure form or mixture, but not $Zn_3(OH)_4(NO_3)_2×2H_2O$, ΔG of which is 37 %. Fig. 5 shows the XRD images of $Cu_{20}Zn_{80}$ (A), $Cu_{40}Zn_{60}$ (B), $Cu_{50}Zn_{50}$ (C), $Cu_{60}Zn_{40}$ (D), and $Cu_{80}Zn_{20}$ (E) samples.

The first diffractogram (A) indicates that $Cu_{20}Zn_{80}$ sample is probably a mixture of $Zn_5$HN and CuHN. The strongest peaks of $Zn_5$HN (at 2θ = 9.2) and CuHN (at 2θ = 12.8) are well expressed. No major characteristic peaks of ZnO or CuO can be found. Li et al. also made this conclusion in an attempt to synthesize mixed Cu-Zn hydroxy nitrates [25]. They have synthesized several Cu-Zn-containing crystals by quick co-precipitation by simultaneously adding KOH and copper nitrate solutions into zinc nitrate solution. Comparing the XRD and FTIR spectra of pure hydroxy nitrates with those of mixed samples, they concluded, that the following reactions take place separately to form two different phases:

$Cu^{2+} + 1.5\ OH^- + 0.5\ NO_3^- = Cu(OH)_{1.5}(NO_3)_{0.5}$

$Zn^{2+}+1.6OH^-+0.4NO_3^-+0.4H_2O=Zn(OH)_{1.6}(NO_3)_{0.4}×0.4H_2O$

At the base of this conclusion is the fact that $K_{sp}$ of CuHN is much lower than that of $Zn_5$HN.

A different conclusion is reached by Ghotbi et al., who synthesized mixed Zn-Cu hydroxy nitrates by co-precipitation of copper and zinc nitrate at pH = 7.0 [16]. According to them, some of $Zn^{2+}$ in $Zn_5$HN are replaced by $Cu^{2+}$ and the incorporation of copper ions within the $Zn_5$HN layers does not change the material structure.

The analysis of the diffraction patterns B C, D and E in Fig. 5 does not confirm the suggestions of Li et al. and Ghotbi et al. [16, 25]. As the copper content of the mixed samples increases, the $Zn_5$HN characteristic peaks weaken and with $Cu_{50}Zn_{50}$ sample disappear completely and only those of CuHN remain. Careful analysis shows no offset of the peaks at higher 2θ angles than those of pure CuHN. This suggests that the peaks observed belong to mixed Zn-Cu hydroxy nitrates with a composition $(Zn_xCu_{2-x})(OH)_3NO_3$ (ZnCuHN). The spectra shown in Fig. 5 allow us to conclude that $Cu_{20}Zn_{80}$ and $Cu_{40}Zn_{60}$ samples are a mixture of $Zn_5$HN and mixed $(Zn_xCu_{2-x})(OH)_3NO_3$. The remaining samples do not contain $Zn_5$HN. They most likely represent pure $(Zn_xCu_{2-x})(OH)_3NO_3$ or a mixture of $(Zn_xCu_{2-x})(OH)_3NO_3$ and $Cu_2(OH)_3NO_3$. In our view, the formation of mixed hydroxy nitrates based on $Zn_5$HN as the host structure is impossible due to the large difference in the solubility of zinc and copper hydroxy nitrates. The reason for the presence of copper in the ZnO obtained after decomposition is the precipitation of mixed fine crystalline $(Zn_xCu_{2-x})(OH)_3NO_3$, whose decomposition leads to the formation of Cu doped ZnO.

The fundamental difference between our results

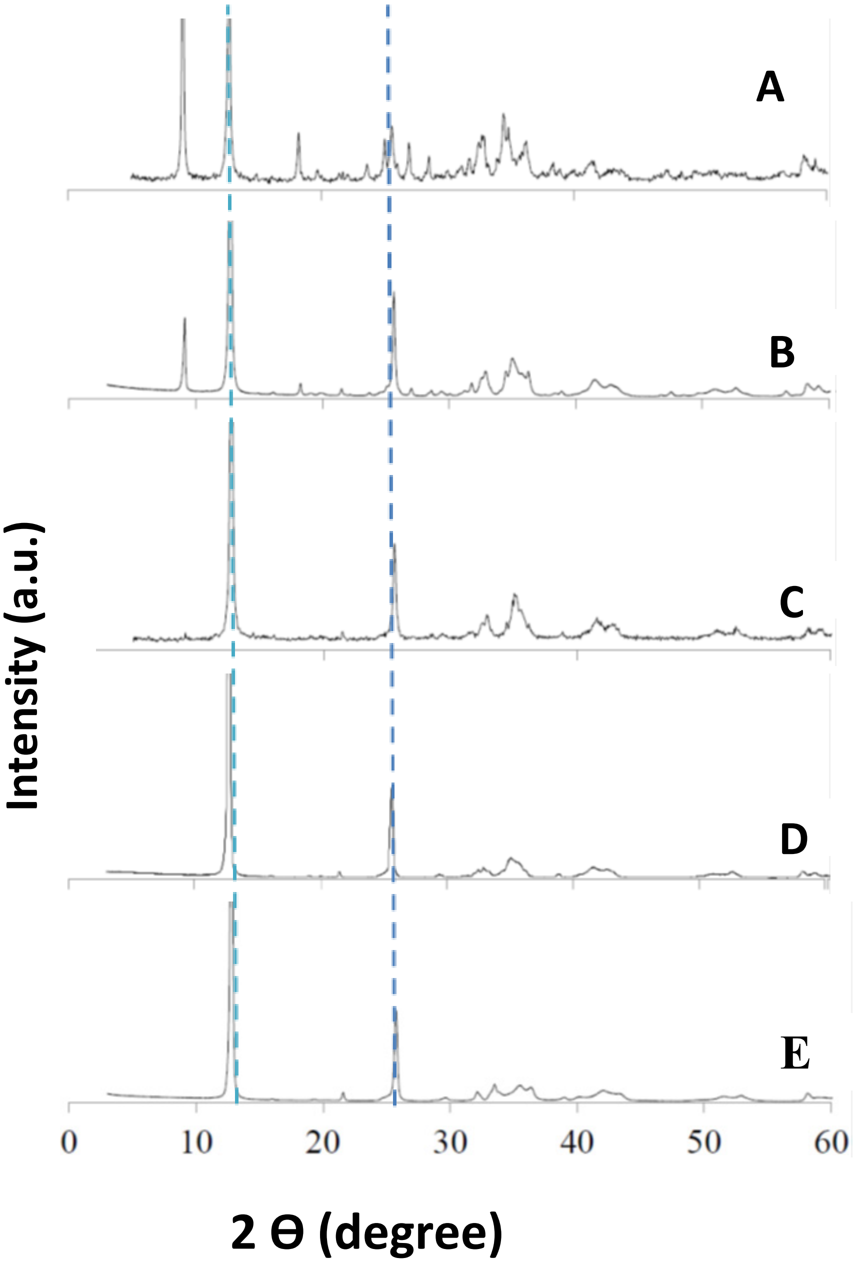


Fig.5 XRD patterns of $Cu_{20}Zn_{80}$ (A), $Cu_{40}Zn_{60}$ (B), $Cu_{50}Zn_{50}$ (C), $Cu_{60}Zn_{40}$ (D), and $Cu_{80}Zn_{20}$ (E) samples.

and those of Li et al. is probably due to the different conditions of the experiment [25]. In our view, low concentrations of starting salts in the Li et al. experiment lead to preferential precipitation of all copper ions as $Cu_2(OH)_3NO_3$, and then precipitation of zinc ions in the form of $Zn_5(OH)_8(NO_3)_2.2H_2O$ [25]. This type of precipitation is described in detail in our earlier study [23].

Taking into account our experience in the field of investigation, in this experiment, we have used concentrated solutions (3.6 M). Under these conditions, the concentration of $Zn^{2+}$ is high, which does not allow preferential precipitation of $Cu_2(OH)_3NO_3$. This assumption is strongly supported by the additional FTIR, SEM and TEM studies. Fig. 6 shows the FT-IR spectra of $Cu_{20}Zn_{80}$ (A), $Cu_{40}Zn_{60}$ (B), $Cu_{50}Zn_{50}$ (C), $Cu_{60}Zn_{40}$ (D), and $Cu_{80}Zn_{20}$ (E) samples.

In all five spectra, a strong and broad absorption due to OH stretching vibration can be observed at

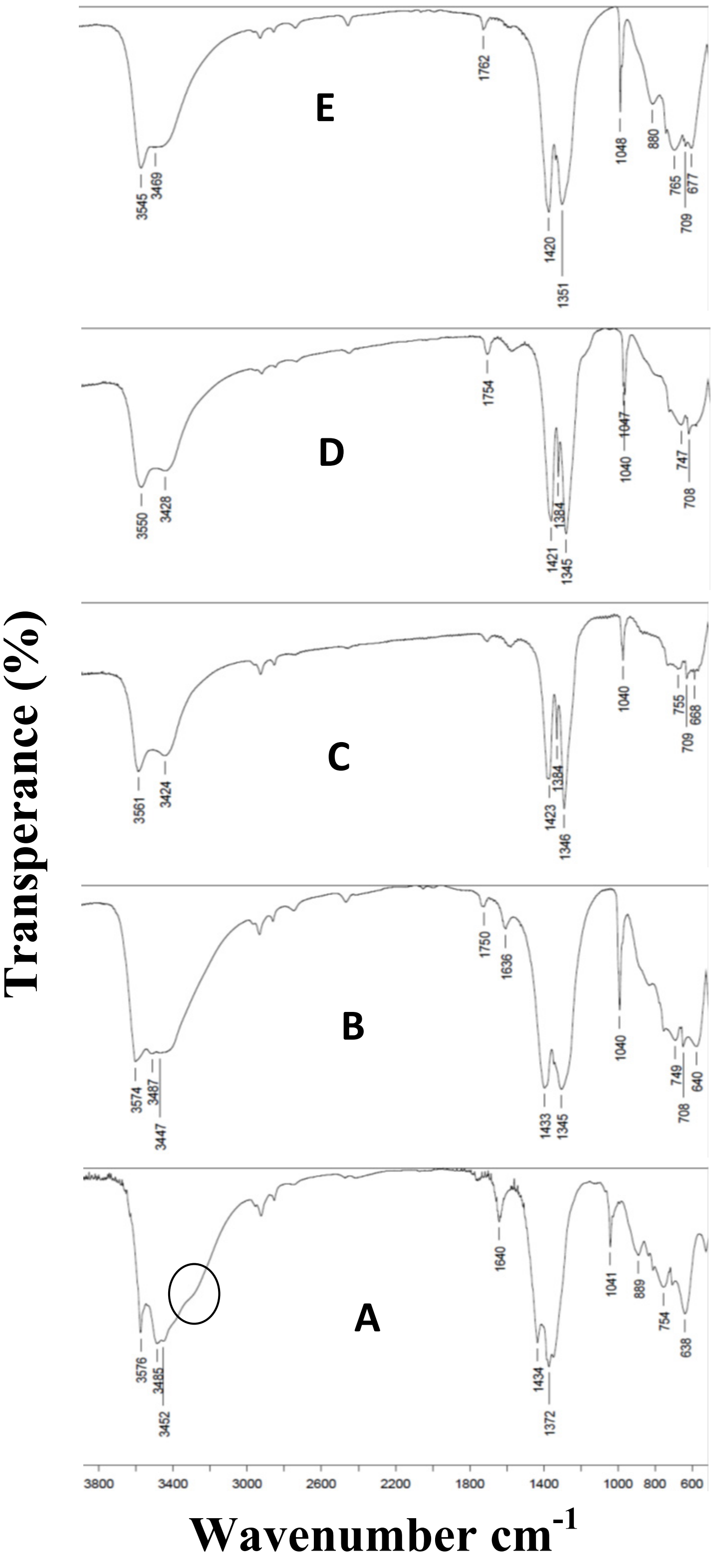


Fig. 6. FT-IR spectra of $Cu_{20}Zn_{80}$ (A), $Cu_{40}Zn_{60}$ (B), $Cu_{50}Zn_{50}$ (C), $Cu_{60}Zn_{40}$ (E), and $Cu_{80}Zn_{20}$ (D) samples.

approximately 3500 $cm^{-1}$. Well expressed absorption bands in the region from 880 $cm^{-1}$ to 1600 $cm^{-1}$, connected with interlayer anion can be seen. The single absorption band at 1640 $cm^{-1}$, characteristic of the presence of water in $Zn_5HN$ is visible only in $Cu_{20}Zn_{80}$ (A) and $Cu_{40}Zn_{60}$ (B) samples which confirms the presence of this compound. The absorption lines around 1428 $cm^{-1}$ and 1341 $cm^{-1}$, typical for asymmetric and symmetric $NO_2$ stretching bands of CuHN, confirm the assumption that these samples are a mixture of $Zn_5HN$ and CuHN. The spectra of the other three samples are practically identical and are very close to the FTIR spectrum of CuHN. The obtained results give us reason to assume that $Cu_2(OH)_3NO_3$ is the host structure of all mixed Zn-Cu hydroxy nitrates contained in the synthesized samples. Fig. 7 shows the DTA, DTG and TG curves of $Cu_{20}Zn_{80}$ (A), $Cu_{40}Zn_{60}$ (B), $Cu_{50}Zn_{50}$ (C), $Cu_{60}Zn_{40}$ (D), and $Cu_{80}Zn_{20}$ (E) samples.

The starting point in our analysis of the results presented in Figs. 7 is the result of sample $Cu_{50}Zn_{50}$ (C). Chemical analysis showed that the precipitation of the two nitrates ($Cu(NO_3)_2.3H_2O$ and $Zn(NO_3)_2.6H_2O$) was complete and the molar ratio Cu/Zn in the sample dried at 65°C was 50/50. The process of its thermal decomposition is one-step and follows that of pure CuHN. This gives us reason to believe that the compound obtained is with the composition $(Cu_xZn_{2-x})(OH)_3NO_3$, where x = 1.0. The decomposition of $Cu_{50}Zn_{50}$ is a one-step process with a weight loss of 33.48 %. This value is very close to the theoretical calculated - 33.47 %. Analysis of the results for the remaining samples leads to the conclusion that this compound is present in all of them together with pure $Zn_5HN$ in the samples with a molar ratio Cu/Zn < 1.0 and pure CuHN in the samples with Cu/Zn > 1.0. Table 4 presents TG data of mixed Cu-Zn hydroxy nitrates.

The thermal decomposition of samples $Cu_{20}Zn_{80}$ and $Cu_{40}Zn_{60}$ (A and B) is a three-step process with a total weight loss of 33.1 and 33.0, respectively. However, the DTG and DTA curves show that the first and the second steps of weight loss are in the temperature range up to 180°C. They are connected with the loos of water (first step) and decomposition of $Zn_5HN$ to $Zn_3HN$ (second step). Taking into account the fact that the weight loss of pure ZnHN in this temperature range is 11.6 % (theoretically two stages of 5.8 %), we can calculate with a high degree of reliability its content in the mixed samples. For the sample with composition $Cu_{20}Zn_{80}$ the content of $Zn_5HN$ is 56.0 %, and in the sample with composition $Cu_{40}Zn_{60}$ - 21.5 %. The remaining 44.0 % and 78.5 % belong to the mixed $(Cu_xZn_{2-x})(OH)_3NO_3$. We suppose that the mixed samples have the composition $(Cu_1Zn_1)(OH)_3NO_3$. The results for $Zn_5HN$, obtained by the thermal analysis, are very close to the theoretical value of 60.8 % at Cu/Zn molar ratio of 20/80 and 20.6 % at Cu/Zn molar ratio 40/60 and support our suggestion.

The third weight loss is related to the simultaneous decomposition of $Zn_3HN$ and the formed mixed hydroxy nitrate. An increase in the Cu/Zn molar ratio leads to a decrease in the weight loss in the first and second stages from 6.5 at $Cu_{20}Zn_{80}$ to 2.5 % at $Cu_{40}Zn_{60}$. This is associated with the reduction of $Zn_5HN$ content and the incorporation of $Zn^{2+}$ in the mixed hydroxy nitrates. Based on the results presented, we can conclude that these two samples are a mixture of $Zn_5HN$ and $(Zn_xCu_{2-x})(OH)_3NO_3$, as most likely x = 1.0.

The thermal decomposition of samples $Cu_{50}Zn_{50}$, $Cu_{60}Zn_{40}$ and $Cu_{80}Zn_{20}$ (C, D and E) is completely different. As noted above, the $Cu_{50}Zn_{50}$ sample is most likely a mixed hydroxy nitrate with a fixed composition $(Zn_{1.0}Cu_{1.0})(OH)_3NO_3$ with one step of thermal decomposition. The decomposition of $Cu_{60}Zn_{40}$ is a one-step process with a weight loss of 32.8 %. The results of the thermal analysis of both samples are very similar.

The results in Fig. 7E strongly indicate that the increasing copper content results in the separation of $Cu_{80}Zn_{20}$ into two compounds. The onset and the edge temperatures (185°C and 254°C) of the first compound are very close to the typical temperatures of the pure $(Cu)_2(OH)_3NO_3$. It is impossible to define the onset temperature of the second compound due to the partial overlap of the two processes, but the edge temperature is the same as that of the other mixed samples. This gives us reason to assume that the second compound has the same composition as the mixed compound of the other samples - $(Zn_1Cu_1)(OH)_3NO_3$. The claim that mixing solutions of copper nitrate and zinc nitrate in an alkaline medium leads to the formation of mixed hydroxy nitrates with the composition $(Zn_xCu_{2-x})(OH)_3NO_3$, where $0 < x < 1.8$ requires the sample $Cu_{80}Zn_{20}$ to be a homogeneous product with the composition $(Zn_{0.2}Cu_{1.8})(OH)_3NO_3$ [23]. The absence of any zinc-containing compound ($Zn_5HN$, $Zn_3HN$, ZnO) in the XRD pattern of the $Cu_{80}Zn_{20}$ sample

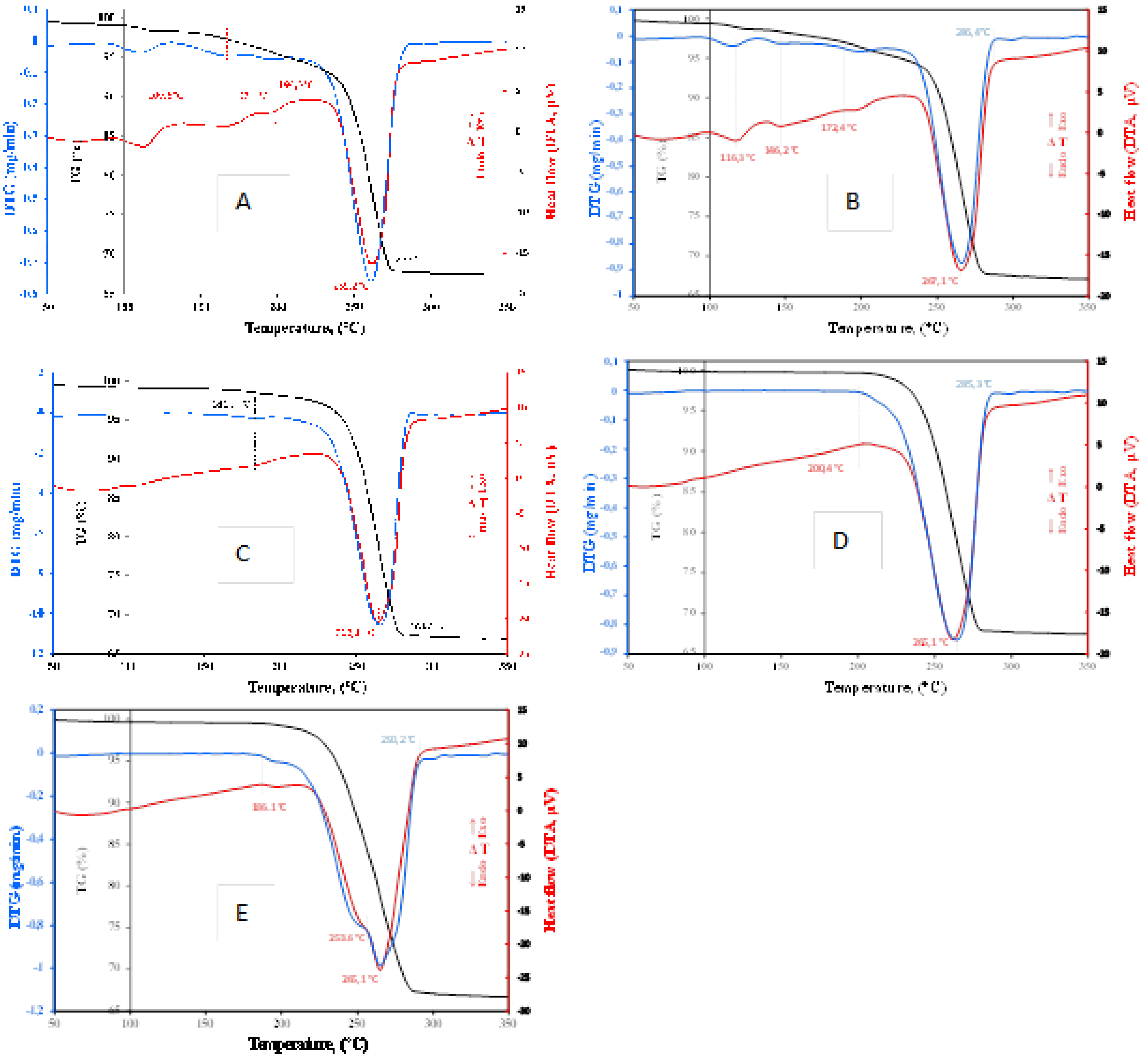


Fig. 7. DTA, DTG and TG curves of $Cu_{20}Zn_{80}$ (A), $Cu_{40}Zn_{60}$ (B), $Cu_{50}Zn_{50}$ (C), $Cu_{60}Zn_{40}$ (D), and $Cu_{80}Zn_{20}$ (E) samples.

Table 4. TG data of $Cu_{20}Zn_{80}$ (A), $Cu_{40}Zn_{60}$ (B), $Cu_{50}Zn_{50}$ (C), $Cu_{60}Zn_{40}$ (E), and $Cu_{80}Zn_{20}$ (D) samples.

| Sample | Cu content, % | | Zn content, % | |
|---|---|---|---|---|
| | Result | Theoretical | Result | Theoretical |
| $Cu_{20}Zn_{80}$HN - approach 1 | 27.80 ± 1.24 | 26.27 | 25.81 ± 1.68 | 27.03 |
| $Cu_{20}Zn_{80}$HN - approach 2 | 26.82 ± 1.20 | | 26.84 ± 1.44 | |
| $Cu_{40}Zn_{60}$HN - approach 1 | 27.46 ± 1.64 | | 25.82 ± 1.84 | |
| $Cu_{40}Zn_{60}$HN - approach 2 | 28.20 ± 1.54 | | 26.86 ± 1.24 | |
| Average | 27.57 ± 0.58 | | 26.33 ± 0.60 | |

confirms our assumption for the formation of a compound with a defined composition $(Zn_1Cu_1)(OH)_3NO_3$ where all zinc atoms are incorporated. Notably, the results for $Cu_{80}Zn_{20}$ sample, prepared by both methods for synthesis are practically identical.

The analysis of the gases released during thermal decomposition (water, NO and $NO_2$) confirm the assumptions made (it is presented only for $Cu_{50}Zn_{50}$). The decomposition of the first two samples ($Cu_{20}Zn_{80}$ and $Cu_{40}Zn_{60}$) is associated with the release of water at all three weight stage losses, decreasing with increasing copper content. The water release correlates with $Zn_5$HN content in the samples. No water was found in the gas products of $Cu_{50}Zn_{50}$, $Cu_{60}Zn_{40}$ and $Cu_{80}Zn_{20}$ samples up to 200°C, which excludes the presence of $Zn_5$HN. NO and $NO_2$ separation is a one-step process for all three samples. Fig. 8 shows the SEM images of $Cu_{20}Zn_{80}$ (A), $Cu_{40}Zn_{60}$ (B), $Cu_{50}Zn_{50}$ (C), $Cu_{60}Zn_{40}$ (D), and $Cu_{80}Zn_{20}$ (E) samples.

The image of sample $Cu_{20}Zn_{80}$ (Fig. 8A) clearly shows sheet-like morphology, typical for pure $Zn_5$HN (nanoplates). Small crystals with a diameter below 0.5 μm, which in our opinion confirm the presence of mixed Zn-Cu hydroxy nitrate, are also noticeable. The results of EDS analyzes ($n = 10$) confirm the presence of two groups of crystals. The crystals of the first group have a content of zinc 86.1 ± 8.2 % and copper 13.9 ± 8.2 %, and the second - with a content of zinc 61.8 ± 2.7 % and a content of copper 38. 2 ± 2.7 %. The exact composition of the crystals cannot be determined due to their small size and the influence of their environment, but with a high degree of reliability, we can say that the first group of crystals belongs to pure $Zn_5$HN and the second to mixed ZnCuHN. The shape of $Cu_{40}Zn_{60}$ sample (Fig. 8B) is featured two groups of sheet-like (probably $Zn_5$HN) and belt-like (probably ZnCuHN) particles with different dimensions. The other three samples are a homogeneous mixture of belt-like crystals with dimensions below 1.0 μm. The sample $Cu_{50}Zn_{50}$ (Fig. 8C) has uniform belt-like morphology which we believe confirms the formation of mixed hydroxy nitrate with the composition $(Zn_1Cu_1)(OH)_3NO_3$. EDS analysis showed that the average crystal composition was 51.0 ± 7.0 % Zn and 49.0 ± 7.1 % Cu. Close to this is the composition of the crystals of the sample $Cu_{60}Zn_{40}$ - 48.6 ± 4.6 % Zn and 51.4 ± 4.8 % Cu.

The presented results of XRD, thermal and IR analysis studies suggest that all mixed Cu-Zn hydroxy nitrates contain $(Zn_1Cu_1)(OH)_3NO_3$ together with pure $Zn_5$HN in the samples with a molar ratio $Cu/Zn < 1.0$ and pure CuHN in the samples with $Cu/Zn > 1.0$. This conclusion contradicts all the results known in the scientific literature, which necessitated additional research and the search for additional indisputable evidence. For this purpose, two samples with the predetermined composition of $Cu_{20}Zn_{80}$HN and $Cu_{40}Zn_{60}$HN were again synthesized and precisely studied.

### Synthesis of $Cu_{20}Zn_{80}$HN

#### *Approach 1*

The solutions of all 3.6 M copper nitrate and a part of the potassium base (corresponding to the precipitation of mixed hydroxy nitrate with a composition $(Zn_1Cu_1)(OH)_3NO_3$) (twice of KOH amount required for the complete precipitation of copper as pure $Cu_2(OH)_3NO_3$) were added simultaneously to the solution of zinc nitrate (3.6 M) at 60°C and constant stirring. The resulting precipitate was filtered, the filtrate was retained and the precipitate was washed and dried at 65°C for 24 hours. Potassium base is added to the separated filtrate until the remaining amount of zinc is completely precipitated as $Zn_5(OH)_8(NO_3)_2.2H_2O$.

#### *Approach 2*

It is carried out in the same manner as approach 1, with the precipitate of mixed hydroxy nitrate remaining in the mother liquor for 24 hours with constant stirring to evaluate the stability of the resulting precipitate in the presence of $Zn^{2+}$ ions. The precipitate is filtered, washed and dried at 65°C. Potassium hydroxide is added to the separated filtrate until the remaining amount of zinc is completely precipitated as $Zn_5(OH)_8(NO_3)_2.2H_2O$.

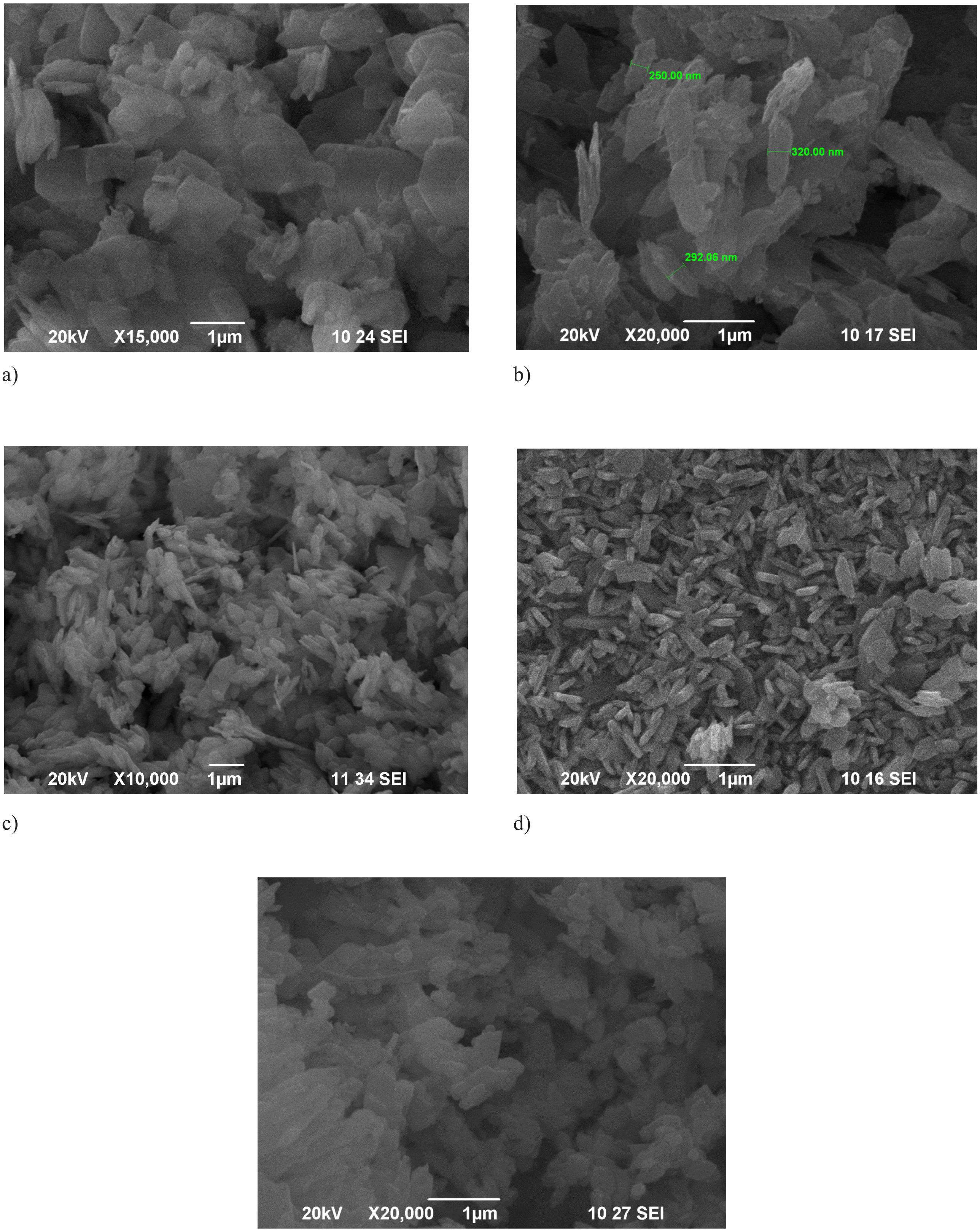
### Synthesis of $Cu_{40}Zn_{60}$HN

The syntheses are carried out in the same way as in the $Cu_{20}Zn_{80}$HN sample, in which case the amount of potassium base in the first stage of the synthesis is two times more (corresponding to the complete precipitation of copper in the form of $(Zn_1Cu_1)(OH)_3NO_3$).

### Analysis of the obtained sludge

#### *Gravimetrically*

The results for the content of $(Zn_1Cu_1)(OH)_3NO_3$ and $Zn_5(OH)_8(NO_3)_2.2H_2O$ in % of the total weight of



a) b) c) d) e)

Fig. 8. SEM images of $Cu_{20}Zn_{80}$ (A), $Cu_{40}Zn_{60}$ (B), $Cu_{50}Zn_{50}$ (C), $Cu_{60}Zn_{40}$ (D), and $Cu_{80}Zn_{20}$ (E) samples.

the precipitates obtained in each synthesis are presented in Table. 5.

If the mixed hydroxy nitrate synthesized during the first stage of the syntheses has a fixed composition and molar ratio Cu/Zn = 1.0, the precipitate of $(Zn_1Cu_1)(OH)_3NO_3$) obtained during the synthesis of the first sample ($Cu_{20}Zn_{80}HN$) should be 39.3 % of the total amount of precipitate, and that of $Zn_5(OH)_8(NO_3)_2.2H_2O$ - 60.7 %. For the second sample ($Cu_{40}Zn_{60}HN$) these values should be 79.5 % and 20.5 %, respectively. The results presented in Table 1 are very close to the theoretical ones, which gives us reason to assume that in all syntheses the whole amount of $Cu^{2+}$ is precipitated in the form of $(Zn_1Cu_1)(OH)_3NO_3$. This composition is stable and remains unchanged after 24 hours in the mother liquor with constant stirring and the presence of a significant amount of $Zn^{2+}$, unprecipitated after the addition of the first portion of KOH. The results of the weight analysis were confirmed by AAS, thermal and XRD analyses. The results for the content of Cu and Zn in the mixed Cu-Zn hydroxy nitrates are presented in Table 6.

The presented in Table 6 results practically coincide with the theoretical ones and confirm the assumption that the molar ratio Cu/Zn in the mixed hydroxy nitrates is 1:1. The samples obtained during the second stage of the synthesis confirm the expectation that they represent pure $Zn_5(OH)_8(NO_3)_2.2H_2O$ and no Cu content was found in them. Fig. 9 shows the results of XRD and thermal analysis of mixed Cu-Zn hydroxy nitrates, prepared following the procedure of approach 2.

The decomposition of both samples is a one-step process with a weight loss of 33.4 % and 33.2 %, respectively. The results of the thermal analysis are very similar to theoretical ones for pure $(Zn_1Cu_1)(OH)_3NO_3$ (33.48 %). No weight loss was found in the temperature region of 50 to 150°C which confirms the absence of $Zn_5HN$, i.e. the entire amount of zinc is included in the composition of the mixed hydroxy nitrate. This is also confirmed by the results of XRD analyzes. Both diffractograms do not contain any of the typical $Zn_5HN$ peaks.

The results in Fig. 9 strongly indicate that the co-precipitation of copper nitrate and zinc nitrate does

Table 5. Content of $(Zn_1Cu_1)(OH)_3NO_3$ and $Zn_5(OH)_8(NO_3)_2\times 2H_2O$ in % of the total weight of the precipitates.

| Sample | Weight loss, % | | |
|---|---|---|---|
| | First | Second | Third |
| | (Weight loss)<br>Onset temp.,°C<br>(Edge temp., °C) | (Weight loss)<br>Onset temp.,°C<br>(Edge temp., °C) | (Weight loss)<br>Onset temp.,°C<br>(Edge temp., °C) |
| $Cu_{20}Zn_{80}$ | (3.1) 90 (110) | (3.4) 138 (167) | (26.6) 181 (260) |
| $Cu_{40}Zn_{60}$ | (1.5) 90 (116) | (1.0) 132 (146) | (30.5) 172 (267) |
| $Cu_{50}Zn_{50}$ | (33.5) 182 (262) | - | - |
| $Cu_{60}Zn_{40}$ | (32.8) 200 (265) | - | - |
| $Cu_{80}Zn_{20}$ | (13.9) 185 (254) | (19.0) - (265) | - |

Table 6. AAS analyses of $Cu_{20}Zn_{80}$ and $Cu_{60}Zn_{40}$ samples (n = 3).

| Sample | $(Zn_1Cu_1)(OH)_3NO_3$, % | | $Zn_5(OH)_8(NO_3)2\times 2H_2O$, % | |
|---|---|---|---|---|
| | Result | Theoretical | Result | Theoretical |
| $Cu_{20}Zn_{80}HN$ - approach 1 | 41.3 | 39.3 | 59.7 | 60.7 |
| $Cu_{20}Zn_{80}HN$ - approach 2 | 39.8 | | 62.2 | |
| $Cu_{40}Zn_{60}HN$ - approach 1 | 80.8 | 79.5 | 19.2 | 20.5 |
| $Cu_{40}Zn_{60}HN$ - approach 2 | 81.2 | | 18.8 | |

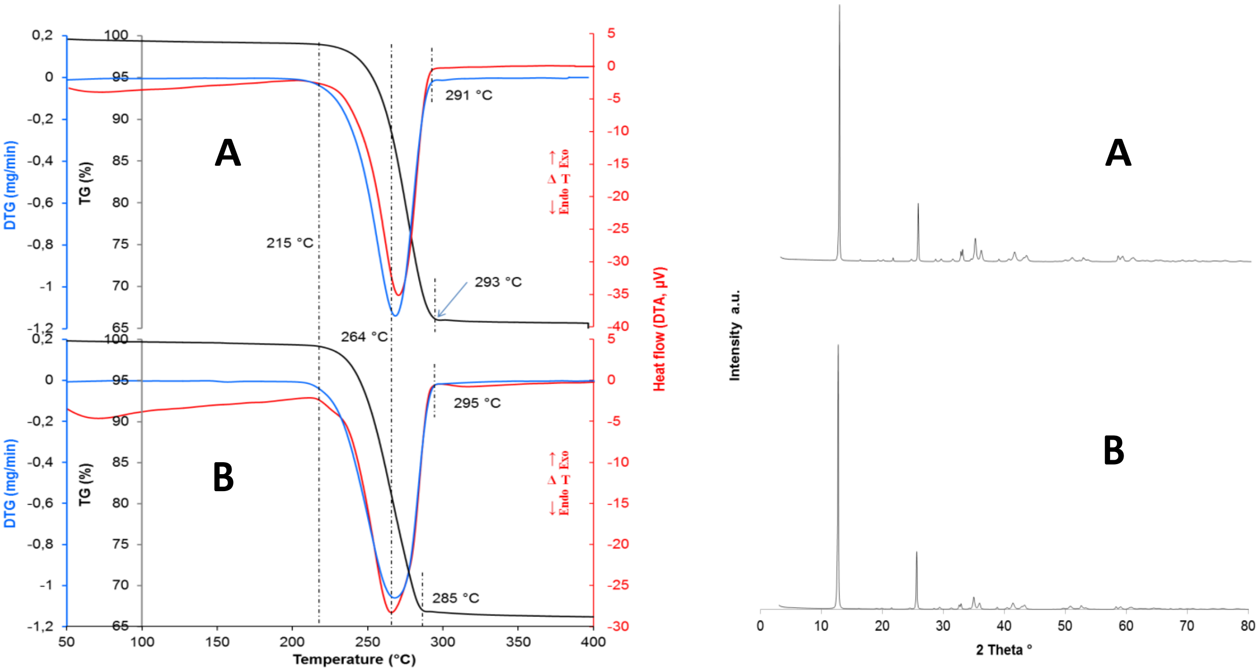


Fig. 9. XRD and thermal analysis of mixed Cu-Zn hydroxy nitrates, prepared following the procedure of approach 2.

not result in a continuous series of solid solutions based on the crystal lattice of $Cu_2(OH)_3NO_3$, but in the formation of the compound with a fixed composition - $(Zn_1Cu_1)(OH)_3NO_3$. The results for the mixed Cu-Zn hydroxy nitrates obtained after precipitation according to approach 1 are identical to those from approach 2.

### Thermal decomposition of mixed Copper-Zinc Hydroxide Nitrates

Our results clearly show that in all cases of copper nitrate and zinc nitrate coprecipitation, the host material in the mixed samples is $Cu_2(OH)_3(NO_3)_2$. On the opposite, in the case of mixed Zn-Cu oxides, prepared by thermal decomposition of mixed Cu-Zn hydroxy nitrates the host material is ZnO. Ghotbi et al. have used a series of layered zinc and copper hydroxide nitrates as precursors to produce pure and copper doped nanostructured zinc oxides [16]. It was found, that the mean crystallite sizes and the lattice parameter values do not show a specific trend with the increase of the doping agent from 2 to10 %. The authors proved that this method is suitable for the synthesis of pure and copper doped zinc oxides with tunable optical band gaps. Thaweesaeng et al. reported the preparation of Cu-doped ZnO nanopowders with up to 5 wt. % Cu by co-precipitation of concentrated (5 M) $Zn(NO_3)_2×6H_2O$ and the proper amount of $Cu(NO_3)_2×3H_2O$ at final pH = 14 [17]. XRD results indicate an ignorable change in ZnO crystal structure with Cu additive in the doped samples with 4 % and 5 % and the mixture of ZnO and CuO at higher Cu doping was proved. Mukhtar et al. have been synthesized nanocrystalline zinc oxide particles doped with $Cu^{2+}$ ions by co-precipitation of $CuSO_4×5H_2O$, $ZnSO_4×7H_2O$ and NaOH, followed decomposition at 200°C for 1 h [36]. Structure analysis indicates that copper ions substitute for zinc ions without changing the ZnO structure. The determined solubility limit of copper in nanocrystalline zinc oxide particles is approximately 11 at. %.

Any data in the literature was found for Zn-doped CuO prepared by thermal decomposition of layered hydroxy salts. The results of XRD analysis synthesized by us ZnHN, CuHN and mixed Cu-Zn hydroxy nitrates after calcination for two hours at 450°C are presented in Fig. 10.

Heating leads to full destruction of the layered structures of all samples and only typical ZnO and CuO peaks can be seen without noticeable offset compared to the peaks of pure oxides. The intensity of the peaks correlates with the composition of the samples. Notably,

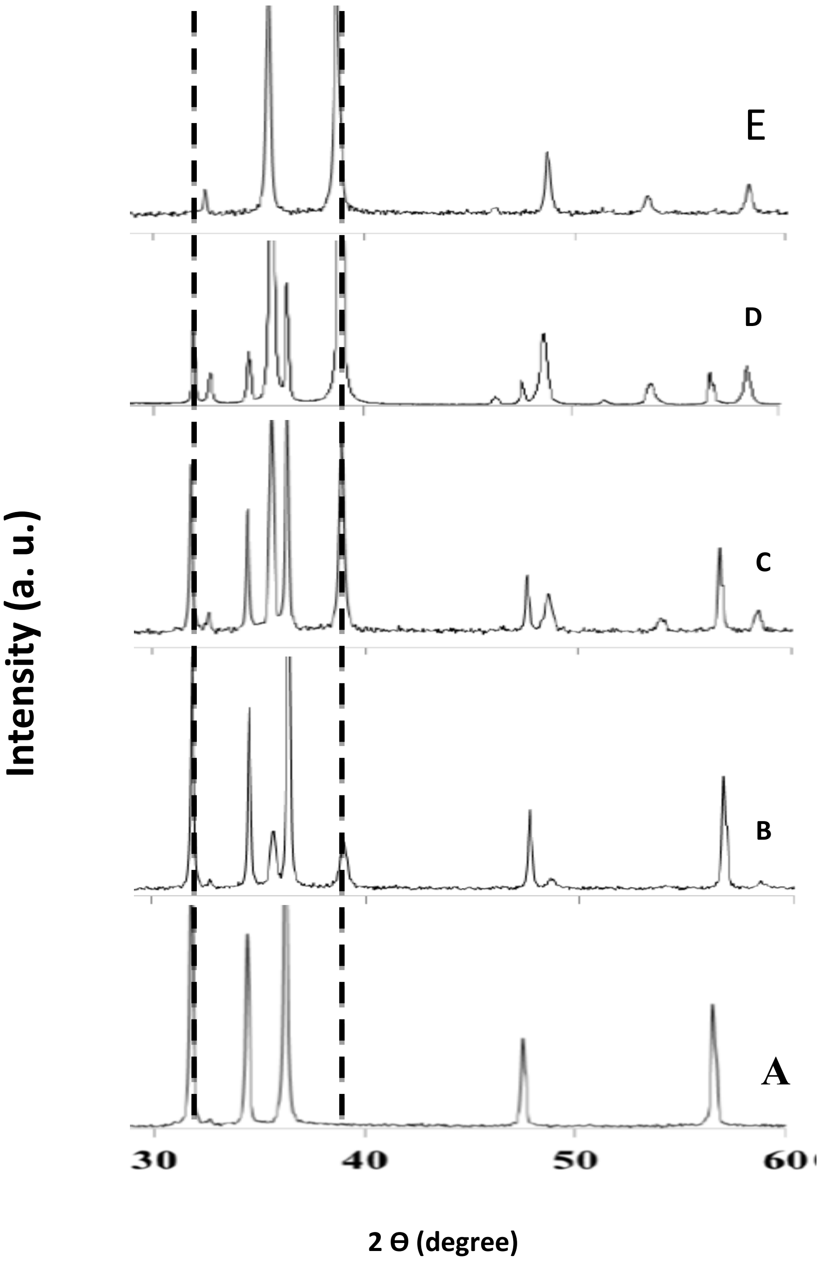


Fig. 10. XRD patterns of pure ZnHN (A), pure CuHN (E) and mixed Cu-Zn hydroxy nitrates with composition $Cu_{20}Zn_{80}$ (B), $Cu_{50}Zn_{50}$ (C) and $Cu_{80}Zn_{20}$ (D) after calcination at 450°C.

both ZnO and CuO are present in all mixed samples. The expectation that the formation of a solid solution in mixed hydroxy nitrates in a wide range will lead to an expansion of the solubility limit of copper in nanocrystalline zinc oxide particles after their thermal decomposition was not justified. This limit is significantly below 20 % and its exact determination for each of the mixed compositions requires further investigations.

## CONCLUSIONS

- A method for control preparation of mixed Cu-Zn hydroxy nitrates by using concentrated solutions of $Cu(NO_3).3H_2O$ and $Zn(NO_3)\times6H_2O$ is developed.
- In all cases of copper nitrate and zinc nitrate coprecipitation, the host material in the mixed samples is $Cu_2(OH)_3(NO_3)_2$. On the opposite, in the

case of mixed Zn-Cu oxides, prepared by thermal decomposition of mixed Cu-Zn hydroxy nitrates the host material is ZnO.

- The composition of the mixed Cu-Zn hydroxy nitrates strongly depends on the molar ratio Cu/Zn in the stock solution. At a molar ratio Cu/Zn < 1.0 the synthesized samples contain $Zn_5(OH)_8(NO_3)_2{\times}2H_2O$ and $(Zn_1Cu_1)(OH)_3NO_3$, and at a molar ratio Cu/Zn > 1.0 - $Cu_2(OH)_3NO_3$ and $(Zn_1Cu_1)(OH)_3NO_3$.
- The result will help to expand the use of nanostructured materials as precursors to produce important for practice mixed nanostructured materials, allowing controlled release of elements and their assimilation by plants.

***Acknowledgements***

*This work was partially supported by the Bulgarian Ministry of Education and Science under the National Research Programme "Healthy Foods for a Strong Bio-Economy and Quality of Life" approved by DCM № 577 / 17.08.2018".*

## REFERENCES

1. J. He, M. Wei, B. Li, Y. Kang, D. Evans, X. Duan, Layered double hydroxides, Springer, Berlin, Heidelberg, 2006.
2. W.K. Ng'etich, B.S. Martincigh, A critical review on layered double hydroxides: Their synthesis and application in sunscreen formulations, Appl. Clay Sci., 208, 106095.
3. M. Rajamathi, G. Thomas, P. Kamath, J. Chem. Sci., 113, 5-6, 2001, 671-680.
4. S.P. Newman, W. Jones, Comparative study of some layered hydroxide salts containing exchangeable interlayer anions, J. Solid State Chem., 148, 1, 1999, 26-40.
5. S. Yamanaka, T. Sako, K. Seki, M. Hattori, Anion exchange reactions in layered basic copper salts. Solid State Ionics, 53, 1992, 527-533.
6. M.Z.B. Hussein, M.Y. Ghotbi, A.H. Yahaya, M.Z. Abd Rahman, The effect of polymers onto the size of zinc layered hydroxide salt and its calcined product, Solid State Sci., 11, 2009, 368-375.
7. N. Ba, L. Zhu, H. Li, G. Zhang J. Li, J. Sun, 3D rod-like copper oxide with nanowire hierarchical structure: Ultrasound assisted synthesis from $Cu_2(OH)_3NO_3$ precursor, optical properties and formation mechanism, Solid State Sci., 53, 2016, 23-29.
8. Hu Xiulan, Preparation method of mesoporous nano flake zinc oxide powder with high specific surface area, CN Patent No103058265A, 2013.
9. R. Saravanan, S. Karthikeyan, V. Gupta, G. Sekaran, V. Narayanan, A. Stephen, Enhanced photocatalytic activity of ZnO/CuO nanocomposite for the degradation of textile dye on visible light illumination, Mater. Sci. Eng. C, 33, 2013, 91-98.
10. B. Li, Y. Hao, B. Zhang, X. Shao, L. Hub, A multifunctional noble-metal-free catalyst of CuO/TiO2 hybrid nanofibers, Appl. Catal. A: Gen., 531, 2017, 1-12.
11. R.N. Mariammal, K. Ramachandran, B. Renganathan, D. Sastikumar, On the enhancement of ethanol sensing by CuO modified $SnO_2$ nanoparticles using fiber-optic sensor, Sens. Actuators B, 169, 2012, 199-207.
12. J. Gajendiran, V. Rajendran, Synthesis and characterization of coupled semiconductor metal oxide (ZnO/CuO) nanocomposite, Mater. Lett, 116, 2014, 311-313.
13. S. Singhal, J. Kaur, T. Namgyal, R. Sharma, Cu-doped ZnO nanoparticles: Synthesis, structural and electrical properties, Physica B, 407, 2012, 1223-1226.
14. H. Liu, J. Yang, Z. Hua, Y. Zhang, L. Yang, Li Xiao, Zhi Xie, The structure and magnetic propertiesof Cu-doped ZnO prepared by sol gel method, Appl. Surf. Sci., 256, 2010, 4162-4165.
15. S.T. Jun, G.M. Choi, Composition dependence of the electrical conductivity of ZnO(n)–CuO(p) ceramic composite, J. Am. Ceram. Soc., 81, 1998, 695-699.
16. M.Y. Ghotbi, N. Bagheri, S.K. Sadrnezhaad, Nanocrystalline copper doped zinc oxide produced from copper doped zinc hydroxide nitrate as a layered precursor, Adv. Powder Technol., 23, 3, 2012, 279-283.
17. N. Thaweesaeng, S. Supankit, W. Techidheera, W. Pecharapa, Structure properties of as-synthesized Cu-doped ZnO nanopowder synthesized by co-precipitation method, Energy Procedia, 34, 2013, 682-688.
18. C.S. Cordeiro, G.C. Arizaga, L.P. Ramos, F. Wypych, A new zinc hydroxide nitrate heterogeneous catalyst

for the esterification of free fatty acids and the transesterification of vegetable oils, Cat. Commun., 9, 11-12, 2008, 2140-2143.

19. S. Kattel, P.J. Ramírez, J.G. Chen, J.A. Rodriguez, P. Liu, Active sites for $CO_2$ hydrogenation to methanol on Cu/ZnO catalysts, Science, 355, 6331, 2017, 1296-1299.
20. Y. Sun, C. Huang, L. Chen, Y. Zhang, M. Fu, J. Wu, D. Ye, Active site structure study of Cu/Plate ZnO model catalysts for $CO_2$ hydrogenation to methanol under the real reaction conditions, J. $CO_2$ Util., 37, 2020, 55-64.
21. F. Arena, K. Barbera, G. Italiano, G. Bonura, L. Spadaro, F. Frusteri, Synthesis, characterization and activity pattern of Cu–ZnO/$ZrO_2$ catalysts in the hydrogenation of carbon dioxide to methanol, J. Cat., 249, 2, 2007, 185-194.
22. R. Yang, X. Yu, Y.I. Zhang, W. Li, N. Tsubaki, A new method of low-temperature methanol synthesis on Cu/ZnO/$Al_2O_3$ catalysts from CO/$CO_2$/$H_2$, Fuel, 87, 4-5), 2008, 443-450.
23. L. Markov, R. Ioncheva, M. Marinov, K. Ivanov, Synthesis and thermal decomposition of Cu (II) - Zn (II) hydroxide nitrate mixed crystals, Mater. Chem. Phys., 26, 5, 1990, 493-504.
24. S. Mtambo, Doctoral dissertation, Faculty of science chemistry department, Bindura University of science education, 2018.
25. P. Li, L. Li, Y. Du, M.A. Hampton, A.V. Nguyen, L. Huang, Z.P. Xu, Potential foliar fertilizers with copper and zinc dual micronutrients in nanocrystal suspension, J. Nanop. Res., 16, 11, 2014, 1-11.
26. C.T. Le, T.M. Ngo, Synthesis of zinc hydroxide nitrate complex by a sol-gel method for use as foliar fertilizers–a scale up approach, Sci. Technol. Devel. J., 19, 3, 2016, 138-145.
27. K. Ivanov, A. Vasilev, A. Mitkov, N. Nguyen, T. Tonev, Application of Zn-containing foliar fertilisers for recovery of the grain productivity potential of Zn-deficient maize plants, Ital. J. Agron., 2021, 1759-1767.
28. K. Rekha, M. Nirmala, M.G. Nair, A. Anukaliani, Structural, optical, photocatalytic and antibacterial activity of zinc oxide and manganese doped zinc oxide nanoparticles, Physica B 405, 2010, 3180-3185.
29. C. Chouillet, J. Krafft, C. Louis, H. Lauron-Pernot, Characterization of zinc hydroxynitrates by diffuse reflectance infrared spectroscopy-structural modifications during thermal treatment, Spectrochim. Acta, Part A, 60, 3, 2004, 505-511.
30. A. Moezzi, P.S. Lee, A.M. McDonagh, M.B. Cortie, On the thermal decomposition of zinc hydroxide nitrate, $Zn_5(OH)_8(NO_3)_2$□$2H_2O$. J. Solid State Chem., 286, 2020, 121311.
31. J.P. Auffredic, D. Louer, A calorimetric study of the thermal decomposition of zinc hydroxy nitrate $Zn_3(OH)_4(NO_3)_2$, Thermochim. Acta 22, 1978, 193-196.
32. I. Schildermans, J. Mullens, B.J. Van der Veken, J. Yperman, D. Franco, L.C. Van Poucke, Preparation and thermal decomposition of $Cu_2(OH)_3NO_3$, Thermochim. acta, 224, 1993, 227-232.
33. C. Henrist, K. Traina, C. Hubert, G. Toussaint, A. Rulmont, R. Cloots, Study of the morphology of copper hydroxyni-trate nanoplatelets obtained by controlled double jet pre-cipitation and urea hydrolysis, J. Cryst. Growth, 254, 2003, 176-187.
34. D. Japić, M. Bitenc, M. Marinšek, Z.C. Orel, The impact of nano-milling on porous ZnO prepared from layered zinc hydroxide nitrate and zinc hydroxide carbonate, Mater. Res. Bull., 60, 2014, 738-745.
35. T. Biswick, W. Jones, A., Pacuła, E. Serwicka, J. Podobinski, The role of anhydrous zinc nitrate in the thermal decomposition of the zinc hydroxy nitrates $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and $ZnOHNO_3 \cdot H_2O$. J. Solid State Chem., 180, 4, 2007, 1171-1179.
36. M. Mukhtar, L. Munisa, R. Saleh, Co-precipitation synthesis and characterization of nanocrystalline zinc oxide particles doped with $Cu^{2+}$ ions, Mater Sci Appl., 3, 2012, 543- 551.