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# DETERMINATION OF THE DEPENDENCE OF THE STRUCTURE OF Zn-Al LAYERED DOUBLE HYDROXIDES, AS A MATRIX FOR FUNCTIONAL ANIONS INTERCALATION, ON SYNTHESIS CONDITIONS

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Layered double hydroxides, especially Zn-Al, are valuable matrices for intercalation with various functional anions: dyes, medicines, food additives, etc. For the purposeful development and optimization of the technology for the synthesis of Zn-Al hydroxides intercalated with functional anions, the phase composition and crystal structure of Zn-Al nitrate layered double hydroxide samples (Zn:Al=4:1) synthesized at solution flow rates of 0.8 and 1.6 l/h, pH=7, 8, 9, 10 and t=10, 20, 30, 40, 50 and 60 °C were studied. XRD showed that all samples synthesized at different temperatures, pH, and solution flow rates were Zn-Al layered double hydroxides with an  $\alpha$ -Zn(OH)<sub>2</sub> crystal lattice of medium crystallinity, with an admixture of an oxide phase with a ZnO lattice. Three sections of the dependence of the crystallite size of the sample on the synthesis temperature were distinguished: 10–20 °C, 30–50 °C, and 60 °C, within which an increase in temperature led to an increase in crystallinity. A hypothesis was put forward about a change in the mechanism or kinetics of LDH formation at temperatures of 30 °C and 60 °C. An increase in the pH of the synthesis and the flow rate of solutions led to an increase in crystallinity.

A retrospective comparative analysis of the phase composition and crystal structure of Zn-Al-nitrate and Zn-Al-tripolyphosphate (tartrazine or Orange Yellow S) LDH samples was carried out. It was found that the use of large and multi-charged functional anions caused significant adsorption on precipitate nuclei and difficult intercalation. As a result, low crystallinity was formed (Tartrazine anion) or a significant part of LDH was decomposed to oxide (tripolyphosphate and Orange Yellow S anions)

**Keywords:** Zn-Al layered double hydroxide, crystallinity, intercalation, nitrate, X-ray diffraction

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## 1. Introduction

Since ancient times, mankind has widely used decorative cosmetics. The composition of these products includes

various components, but pigments are the obligatory and most important of them [1, 2]. These pigments can be obtained both from natural sources and synthetically. The most common mineral pigments are salt and oxide substances, for

example, cobalt-chromium oxide pigments [3], as well as spinel [4, 5], and pigments with the structure of various silicates [6, 7]. Inorganic pigments have high color stability though they have a limited range of colors. Organic pigments are characterized by a wide range of colors, but have low stability to sunlight.

Organic-inorganic hybrid materials combine the advantages of both organic and inorganic pigments. Among pigments of this type, the most promising are layered double hydroxides (LDH) [8] intercalated with anionic dyes [9, 10].

The combination of various metal cations and anionic dyes of various colors in the composition of LDH will significantly expand the color palette of cosmetic pigments. For example, Zn-Al and Acid Yellow 17 [11], Mg-Al and o-Methylene Red [12], Ni-Fe and o-Methylene Red [13], Zn-Al and Mordant Yellow 3 [14, 15], Zn-Al and Acid Yellow 3 [16], Zn-Al and Acid Green bianion 28 [17] are used.

Some authors describe intercalated pigments as nanocomposites. However, it is known that composite materials (organic-organic [18] or inorganic-inorganic [19]) consist of a matrix and a filler, between which there is always an interface. However, intercalated LDH pigments are mainly monophasic substances, so their description as nanocomposites is incorrect.

LDH was also used to purify wastewater from anionic dyes by ion exchange to obtain dye-intercalated LDH. In particular, Evans Blue was extracted using Zn-Al LDH [20], and orange-type dyes were extracted using Zn-Al LDH [21]. Various azo dyes [22], including Remazol Brilliant Violet [23], were extracted using Ni-Al LDH, blue dyes (including Maya Blue) [24] were extracted using Zn-Al LDH, Methyl Orange [25] – using Zn-Al LDH. Amarant [26] was removed from wastewater with Mg-Al LDH, Acid Yellow 42 [27] with Mg-Al LDH, Congo Red [28] with Ni-Al LDH, and Indigo Carmine [29] with Mg-Fe LDH.

It is promising to use LDH as a nanocontainer for special functional anions, such as medicines [30, 31], dye anions [32], sensor anions [33] (like other ion-exchange substances [34]), corrosion inhibitors [35], biologically active additives [36], food additives [37, 38], etc.

The data presented indicate that it is promising to study the characteristics of LDHs for further synthesis of various-purpose functional materials on their basis.

## 2. Literature review and problem statement

Hydroxides of divalent metals (except for alkaline earth metals) are characterized by polymorphism and their two modifications have been described.  $\beta$ -modification (chemical formula  $\text{Me}(\text{OH})_2$ , brucite structure) and  $\alpha$ -modification (chemical formula  $3\text{Me}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , hydrotalcite structure). Structures intermediate between the  $\alpha$ - and  $\beta$ -forms were described for nickel hydroxide [39]. The paper [40] described the formation of  $\text{Ni}(\text{OH})_2$  with a mixed layered ( $\alpha+\beta$ ) structure.

Layered double hydroxide (LDH) is an  $\alpha$ -modification of the host metal hydroxide, in the crystal lattice of which some of the host metal cations are replaced by guest metal cations: for example,  $\text{Zn}^{2+}$  (a host) is replaced by  $\text{Al}^{3+}$  (a guest). Because of this, an excess positive charge is formed in the crystal lattice, which can be compensated by the intercalation of additional anions into the interlayer space. Such anions can be anions of precursor salts. However, anions with spe-

cial functional properties are purposefully intercalated into LDH structures most often. Stabilizing [41] or activating anions [42, 43] can be introduced into the LDH composition.

In this case, the LDH structure includes the following main components [44]: host metal cations, guest metal cations, and intercalated anions. With a purposeful selection of all three components, it becomes possible to design an LDH with the required characteristics.

The development of a functional material based on intercalated LDH consists of the following stages: choosing the type of LDH (a host metal cation and a guest metal cation), choosing the intercalated anion, as well as choosing the synthesis method and conditions.

For the synthesis of materials based on LDH, the use of  $\text{Zn}^{2+}$  as a host metal cation is the most promising. In the synthesis of pigments based on LDH, the advantage of Zn hydroxide is its white color, so Zn LDH is a good basis for a clear development of the color of the intercalated dye. LDH as a base must be health-friendly for use in cosmetics, as a dietary supplement or medicine. The review paper [45] showed the minimal toxicity of Zn-Al LDH.

$\text{Al}^{3+}$  is most often used as a guest metal cation. This is due to high structure-forming and stabilizing properties with respect to the  $\alpha$ -modification of LDH.

The choice of a functional component for obtaining LDH-based materials is based on the nature of the substance. The dye must be anionic for intercalation into the interlayer space of LDH.

The synthesis method and conditions directly determine the micro- and macrostructure of LDH particles. Hydroxides can be prepared by chemical precipitation by direct synthesis (adding an alkaline solution to a metal salt solution) [46, 47], reverse synthesis (adding a metal salt solution to an alkali solution) [48, 49], and the sol-gel method [50]. Also, two-stage high-temperature synthesis [51] and homogeneous precipitation [52] can be used for the synthesis. Electrochemical methods are used to obtain them: cathodic template synthesis [53, 54] and synthesis in a slit diaphragm electrolyzer [55]. However, not all of the above methods can be used for the synthesis of LDH intercalated with functional anions. There are two types of methods for obtaining such materials.

The first one is a two-stage type. It includes:

1) the LDH synthesis with inorganic anions (mainly anions of precursor salts) by reverse precipitation [11, 16, 17], precipitation at constant pH [9, 26], homogeneous precipitation [22], etc.;

2) intercalation of a functional anion by ion-ion exchange.

One of the variants of the two-stage type is the method of LDH reduction from LDO (layered double oxide obtained by LDH calcining) in the presence of a functional anion, for example, a dye anion [12]. The disadvantages of the two-stage methods are the duration of the ion exchange, as well as the need for the synthesis of LDH with anions that can be easily exchanged for functional anions. However, such methods are technologically poorly applicable in production due to complexity, high duration, and high cost.

The second is a one-stage type of preparation. In this case, the formation of dye-intercalated LDH occurs directly during the synthesis. For this purpose, the method of coprecipitation by reverse synthesis or synthesis at a constant pH is used [56, 57]. Direct synthesis is the most promising.

It should be noted that both the amount of the functional intercalated substance and the properties of the intercalated LDH will be primarily determined by the characteristics of

the matrix – LDH. Such a matrix is an LDH intercalated with anions of precursor salts. However, the characteristics of such LDHs as matrices were studied mainly for hydroxides containing catalytically, photocatalytically, and electrochemically active cations (for example, Ni-Al-nitrate LDHs [46]). The characteristics of Zn-Al-NO<sub>3</sub> LDH obtained by different methods and under different conditions are practically not studied because this LDH is not a valuable functional material. At the same time, in [56, 58] for intercalated Zn-Al LDH, and in [59] for Zn-Co LDH, the phenomenon of partial decomposition of the hydroxide phase to the oxide one was found, which could reduce the amount of intercalated anion. Obtaining information on the effect of preparation conditions on the characteristics of Zn-Al-nitrate LDH will make it possible to consciously choose the method and conditions for the synthesis of LDH intercalated with various functional anions.

### 3. The aim and objectives of the study

This work aims to study the effect of synthesis conditions on the structural characteristics of Zn-Al nitrate layered double hydroxide as a matrix for the functional ion intercalation process.

To achieve the aim, the following objectives were set:

- to investigate the phase composition and crystal structure of samples of Zn-Al-nitrate layered double hydroxide synthesized at different temperatures;
- to investigate the phase composition and crystal structure of samples of Zn-Al-nitrate layered double hydroxide synthesized at different pH;
- to investigate the phase composition and crystal structure of samples of Zn-Al-nitrate layered double hydroxide synthesized at different solution flow rates;
- to carry out a retrospective comparative analysis of the phase composition and crystal structure of samples of Zn-Al-nitrate LDHs and Zn-Al LDHs intercalated with various functional anions provided they are obtained under the same conditions (according to previously published works).

### 4. Research materials and methods

#### 4.1. Method of sample preparation

For the synthesis, we used crystalline hydrates of zinc and aluminum nitrates (purified grade). NaOH was used in a granular form with a higher grade (reagent grade).

For the synthesis of Zn-Al-nitrate LDH samples, we used the chemical addition method with maintaining a constant pH, described in [55, 57]. The LDH was synthesized by separately supplying two solutions using peristaltic pumps (the first solution was Zn(NO<sub>3</sub>)<sub>2</sub>+Al(NO<sub>3</sub>)<sub>3</sub> with a molar ratio of Zn:Al=4:1 and the second solution was NaOH, each with a volume of 500 ml) with at the same speed into a 2L beaker containing 100 ml of mother solution. Variable synthesis conditions:

- pH – 7, 8, 9, 10;
- *t* – 10, 20, 30, 40, 50 and 60 °C;
- solution flow rate 0.8 and 1.6 l/h.

Sample marking: **Zn-Al-0.8-8-10**, where **Zn-Al** is the LDH type, **0.8** is the solution flow rate (l/h), **8** is the synthesis pH, and **10** is the synthesis temperature (°C). During the synthesis, the amount of alkali was calculated both for the LDH formation and for maintaining the required pH. The initial solution was prepared with a pH corresponding to

the pH of the synthesis. The synthesis was carried out with continuous stirring, which continued while maintaining the synthesis temperature for 60 minutes after the completion of the addition of solutions. This exposure was necessary for the crystallization process to proceed [58, 59]. After that, the LDH precipitate was filtered off from the mother liquor under a vacuum. Due to the closed-cell composite structure of LDH, a two-stage procedure was used for effective rinsing from soluble salts: the first drying at 70 °C for 24 hours, grinding, soaking in distilled water, filtering, and the second drying under the same conditions. Before studying the characteristics, LDH samples were additionally ground in an agate mortar and sifted through a 71 μm sieve.

#### 4.3. Methods of studying the characteristics of LDH samples

*Study of the characteristics of the synthesized pigment samples.*

The crystal structure of the samples was studied by X-ray diffraction (XRD) using a DRON-3 diffractometer (Russia) (Co-K<sub>α</sub> radiation, angle range 10–90° 2Θ, scanning rate 0.1°/s). The phase composition was determined using international databases. For LDH samples, the size of the crystallite (the size of the coherent scattering region) for the (001) plane was calculated from the diffraction patterns.

XRD of the ZnO powder was carried out for control. The diffraction pattern is shown in Fig. 1.

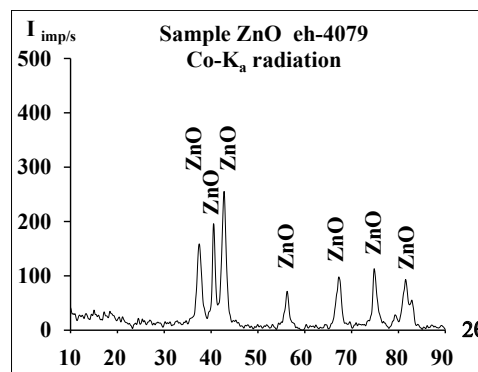


Fig. 1. Diffraction pattern of the ZnO sample

It should be noted that the most characteristic feature of zinc oxide in the diffraction pattern is a triple peak at 2Θ=37.4° (100), 40.6° (002), and 42.8° (101).

### 5. Results of studying the structural characteristics of the Zn-Al-nitrate layered double hydroxide samples

#### 5.1. Results of studying the effect of synthesis temperature

The results of XRD are shown in Fig. 2.

The diffraction patterns of the samples obtained at different temperatures (Fig. 2, *a–f*) showed the peaks of the Zn(OH)<sub>2</sub> lattice corresponding to the Zn-Al LDH. The diffraction pattern showed a peak at 2Θ=41°, corresponding to both ZnO and LDH (with the Zn(OH)<sub>2</sub> lattice) for all samples. A clear dependence of LDH crystallinity (crystallite size) on the synthesis temperature was not revealed; the lowest crystallinity was typical for the samples obtained at 30 °C and 60 °C.

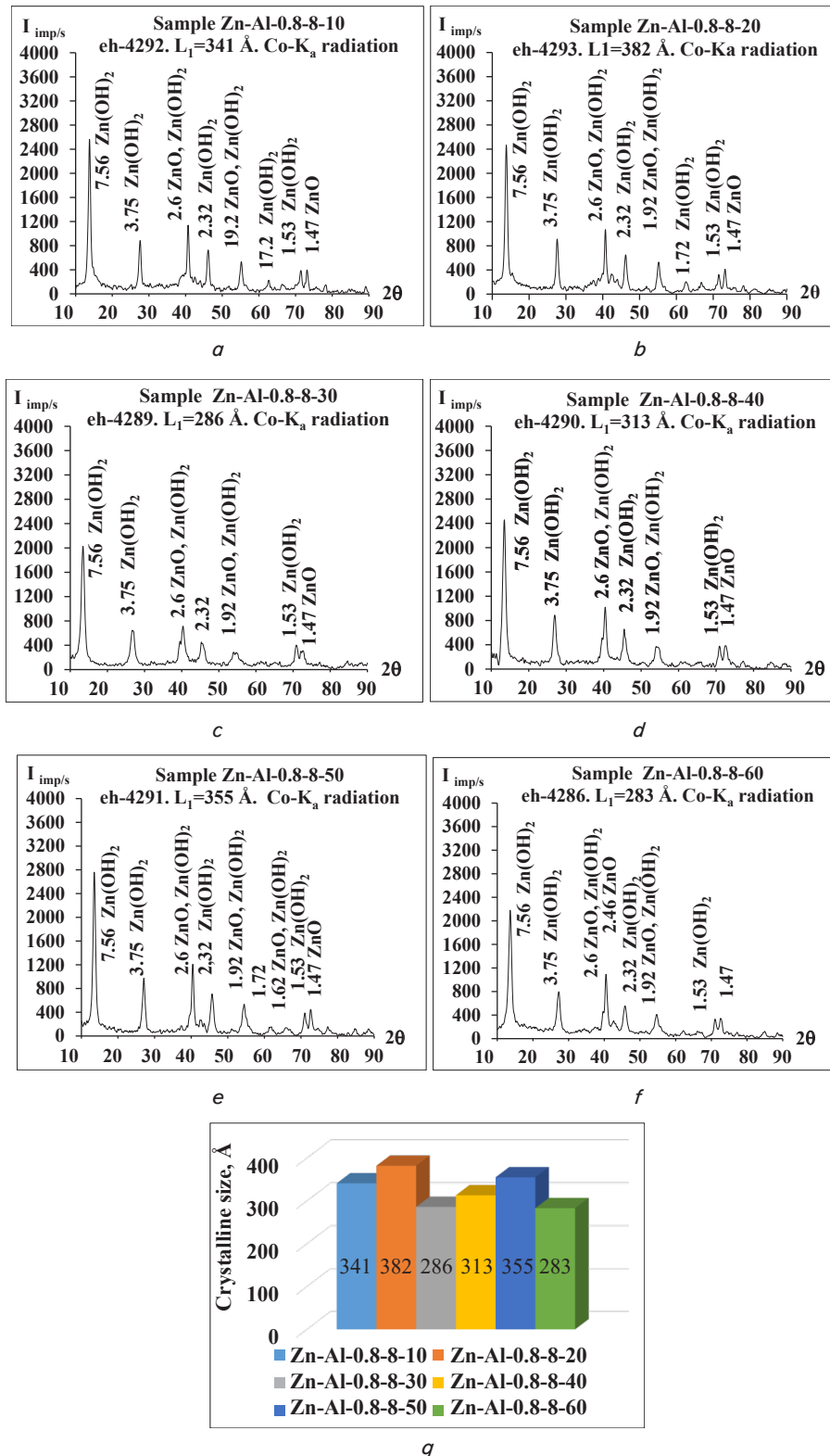


Fig. 2. XRD results for the samples obtained at different temperatures.

Diffraction patterns: *a* – Zn-Al-0.8-8-10, *b* – Zn-Al-0.8-8-20, *c* – Zn-Al-0.8-8-30, *d* – Zn-Al-0.8-8-40, *e* – Zn-Al-0.8-8-40, *f* – Zn-Al-0.8-8-60, *g* – crystallite sizes for the (001) plane, calculated from diffraction patterns

## 5. 2. Results of studying the effect of synthesis pH

The results of XRD are shown in Fig. 3.

The diffraction patterns of the samples obtained at different pH revealed clearly defined peaks of the  $\text{Zn}(\text{OH})_2$  crystal lattice, which corresponded to Zn-Al LDH. The diffraction patterns also showed peaks at  $2\theta=41^\circ$  and  $56^\circ$ ,

which were inherent both in the oxide phase of the ZnO type and in the hydroxide phase of the LDH. It should be noted that the peak at  $2\theta=41^\circ$  was single. It was found that with an increase in the pH of the synthesis, the crystallite size increased monotonically, which indicated an increase in crystallinity.

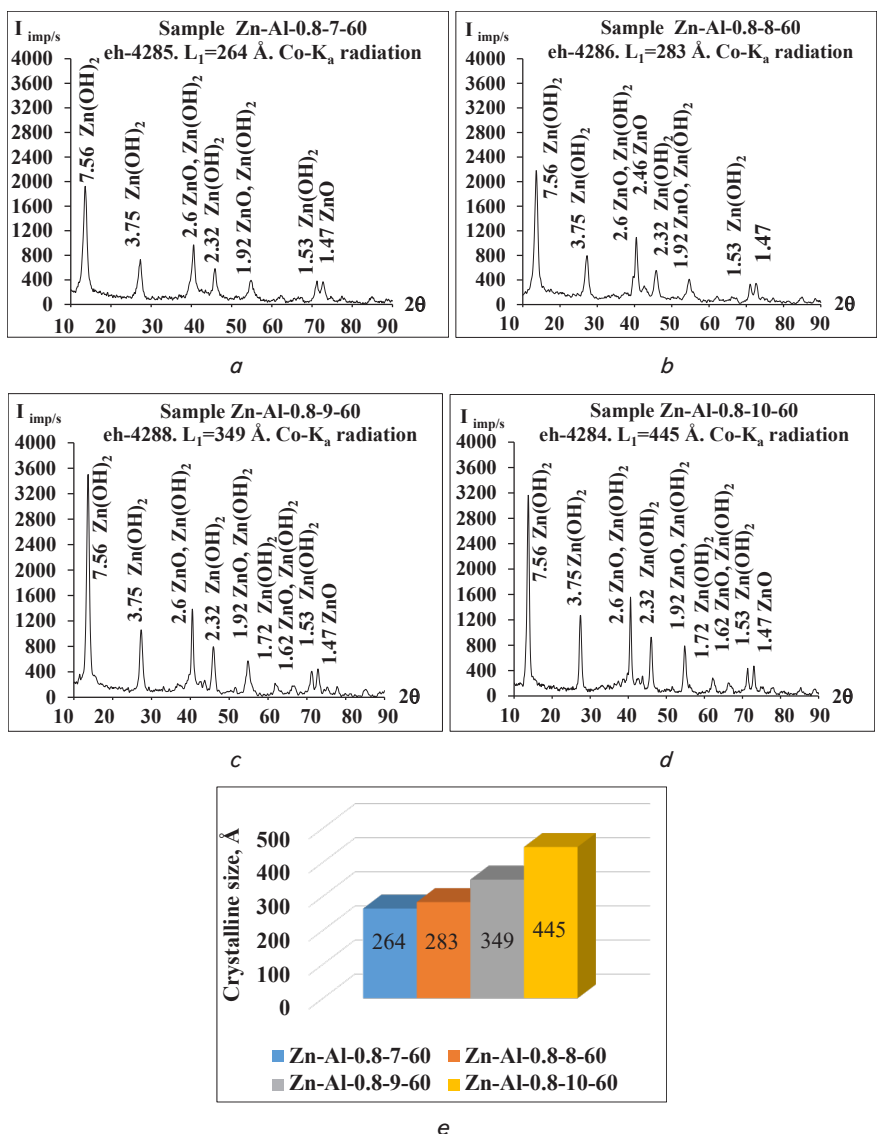


Fig. 3. XRD results for the samples obtained at different pH. Diffraction patterns: *a* – Zn-Al-0.8-7-60, *b* – Zn-Al-0.8-8-60, *c* – Zn-Al-0.8-9-60, *d* – Zn-Al-0.8-10-60, *e* – crystallite sizes for the (001) plane, calculated from diffraction patterns

### 5. 3. Results of studying the effect of solution flow rate

The results of XRD are shown in Fig. 4.

With a twofold increase in the flow rates of the solution from 0.8 g/h (Fig. 4, *a*) to 1.6 l/h (Fig. 4, *b*), the phase composition of the sample did not change, the main component

was the Zn-Al LDH with the  $Zn(OH)_2$  lattice. There were also signs of the presence of a zinc oxide phase on the diffraction patterns. In this case, an increase in the solution flow rate led to an increase in crystallinity: the crystallite size increased from 283  $\text{\AA}$  to 332  $\text{\AA}$ .

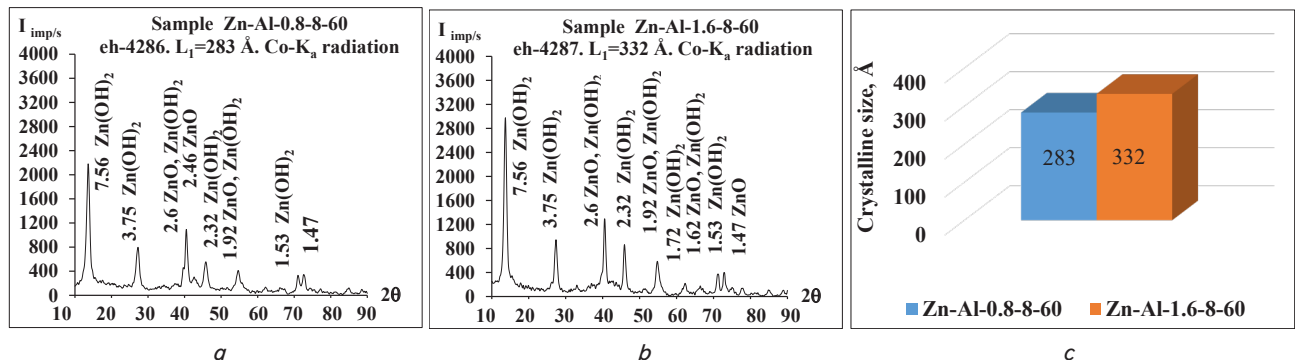


Fig. 4. XRD results for the samples obtained at different solution flow rates. Diffraction patterns: *a* – Zn-Al-0.8-8-60, *b* – Zn-Al-1.6-8-60, *c* – crystallite sizes for the samples calculated from diffraction patterns

## 6. Discussion of the results of studying the characteristics of Zn-Al layered triple hydroxides samples

When discussing the effect of synthesis parameters on the LDH structure, it should be noted that the formation of divalent metal hydroxides proceeds according to a complex mechanism [60]. During the formation of zinc hydroxide (as a guest hydroxide that forms the LDH crystal lattice), the rate of nucleation (formation of crystal nuclei) is significantly higher than the rate of crystal growth. As a result, LDH particles are formed according to a two-stage mechanism [60]:

- 1<sup>st</sup> stage (having a high speed) – formation of nuclei, sticking together with the formation of a primary amorphous particle;
- 2<sup>nd</sup> stage (having a low speed) – crystallization (aging) of the primary amorphous particle. The rate of the crystallization process is determined by the composition of the mother liquor, the duration of the process, and especially the temperature.

It should be pointed out that zinc hydroxide has a high proportion of the covalence of the Zn-OH bond, which leads to partial dehydration of the hydroxide to oxide even at low temperatures.

To analyze the phase composition of Zn-Al LDH samples, a zinc oxide sample was used as a reference sample. Analysis of the diffraction pattern of this sample (Fig. 1) revealed that it was necessary to use a complex of three peaks at  $2\Theta=37.4^\circ$  (plane 100),  $40.6^\circ$  (plane 002), and  $42.8^\circ$  (plane 101) as characteristic peaks of zinc oxide.

*Effect of synthesis temperature.* Analysis of the XRD results (Fig. 2) showed that the main phase of all samples synthesized at temperatures of 10–60 °C had the  $\alpha$ -Zn(OH)<sub>2</sub> crystal lattice with a characteristic peak at  $2\Theta=14^\circ$ . In this case, it was shown that the samples were exactly Zn-Al-nitrate LDH. The diffraction patterns of all samples revealed a peak at  $2\Theta=40.6^\circ$ , which corresponded to both ZnO and Zn(OH)<sub>2</sub>. However, of the three characteristic peaks of ZnO (Fig. 1), only one peak was pronounced clearly in the diffraction patterns of LDH samples (Fig. 2). Most likely, it corresponded not to zinc oxide, but zinc hydroxide. However, a more thorough analysis revealed very weak peaks of zinc oxide at  $2\Theta=37.4^\circ$  and  $42.8^\circ$ . This indicated the presence of a very small amount of the X-ray amorphous phase of zinc oxide in the samples. Crystallite size data for the (001) plane showed that all samples had medium crystallinity. Theoretically, as the temperature increases, the crystallinity of the samples should increase, since with an increase in temperature, the rate of crystallization of the precipitate increases. However, a clearly expressed unambiguous dependence of the crystallite size on temperature was not revealed (Fig. 2, g). It should be noted that the dependence of the crystallite size on temperature can be divided into three sections:

- 1) 10 °C – 20 °C (Zn-Al-0.8-8-10, Zn-Al-0.8-8-20 samples);
- 2) 30 °C – 40 °C – 50 °C (Zn-Al-0.8-8-30, Zn-Al-0.8-8-40, Zn-Al-0.8-8-50 samples);
- 3) 60 °C (Zn-Al-0.8-8-60 sample).

The theoretically predicted increase in crystallinity with increasing synthesis temperature appeared in the first and second sections (Fig. 2, g). It was hypothesized that at temperatures of 30 °C and 60 °C there was a change in the mechanism of nucleation or the formation of primary amorphous particles.

*Effect of synthesis pH.* Analysis of the XRD results of the samples obtained at different alkalinity (Fig. 3) showed that the phase composition of the samples was similar to the previous series (obtained at different temperatures). These

samples were also Zn-Al-nitrate LDH, with an insignificant admixture of the oxide phase.

The data on the crystallite size for the (001) plane (Fig. 3, e) showed that all samples had a medium crystallinity. It was found that with an increase in pH, the crystallinity increased (crystallite size for the (001) plane). This fact is explained by an increase in the rate of crystallization of the primary amorphous particle in the presence of an excess of one of the ions that made up the precipitate in the mother liquor. At the same time, an increase in pH from 7 to 8 (per unit) increased the crystallite size by 7.2 %, while an increase in pH from 9 to 10 increased the crystallite size by 21.6 %. This fact is due to the logarithmic nature of the pH value.

*Effect of solution flow rate.* The XRD results (Fig. 4) showed that an increase in the solution flow rate did not change the crystal structure and phase composition of the samples: Zn-Al-nitrate LDH, with an admixture of the oxide phase.

The data on the crystallite size for the (001) plane (Fig. 4, c) revealed an increase in crystallinity with an increase in the solution flow rate. Increasing the solution flow rate should theoretically increase the rate of nucleation, which should reduce the crystallinity. The data obtained contradicted the theoretical assumptions. The reasons for this phenomenon need to be studied further.

*Retrospective comparative analysis of the phase composition and crystal structure of Zn-Al-nitrate LDH and Zn-Al LDH samples intercalated with various functional anions.* To analyze the phase composition and crystal structure, we chose Zn-Al LDH (with a molar ratio of Zn:Al=4:1) synthesized at pH=8 and a temperature of 60 °C. In this study, a Zn-Al-0.8-8-60 sample was taken for analysis. The following samples were taken as functionally intercalated Zn-Al LDHs: Zn-Al tripolyphosphate LDH (smart anti-corrosion pigment) [35], Zn-Al-Tartrazine LDH [56], and Zn-Al-Orange Yellow S LDH [58] (color pigments). A comparative analysis showed that the nitrate-intercalated Zn-Al-0.8-8-60 sample was Zn-Al LDH of medium crystallinity with a small admixture of the oxide phase. At the same time, the diffraction patterns of the tripolyphosphate intercalated sample [35] and the sample intercalated with the Orange Yellow S dye [58] revealed three characteristic peaks of the zinc oxide phase (possibly Zn-Al layered double oxide). At the same time, the LDH peak was rather weak. This indicated that these samples were biphasic and contained the oxide phase as the main component. The Tartrazine-intercalated sample [56] had a very low crystallinity with indistinct lattice peaks of both ZnO and Zn(OH)<sub>2</sub>. Most likely, the nitrate anion, which had a small size and low charge, was rapidly adsorbed on the emerging nuclei and rapidly intercalated into the interlayer space of the LDH crystal lattice during aging. At the same time, the five-charge tripolyphosphate anion and the two-charge anion dye Orange Yellow S of large size are actively sorbed on the surface of the nuclei, preventing their growth and aggregation. At the second stage, during crystallization, these anions were likely to intercalate much more slowly into the LDH lattice, reducing their stability and increasing the tendency for LDH to decompose to an oxide component. The presence of a significant amount of the oxide phase led to a sharp decrease in the content of the functional anion in the sample. The triple-charged tartrazine anion was also easily adsorbed on the surface of the nuclei. At the same time, this anion was probably more easily intercalated during crystallization, which led to the formation of a low-crystalline structure. It should be concluded that the nature (primarily the charge

and size) of the intercalated anion had a significant effect on the phase composition and crystal structure of the intercalated Zn-Al LDH. It should also be pointed out that to prevent the decomposition of LDH to LDO, it is recommended to reduce the synthesis temperature.

For a more correct prediction of the conditions for the synthesis of Zn-Al LDH, this study should be supplemented by determining the technological characteristics, in particular, the yield and filtering ability, for Zn-Al-nitrate LDH samples synthesized under various conditions.

## 7. Conclusions

1. The phase composition and crystal structure of Zn-Al nitrate layered double hydroxide samples obtained by the synthesis method at a ratio of Zn:Al=4:1, a solution flow rate of 0.8 l/h, pH=8, and temperatures of 10, 20, 30, 40, 50, 60 °C have been studied. It has been shown that all samples are Zn-Al LDHs with the  $\alpha$ -Zn(OH)<sub>2</sub> crystal lattice of medium crystallinity, with an admixture of the oxide phase with the ZnO lattice. On the dependence of the crystallite size on the synthesis temperature, three sections have been distinguished: 10–20 °C, 30–50 °C, and 60 °C, within which an increase in temperature leads to an increase in crystallinity. A hypothesis has been put forward about a change in the mechanism or kinetics of LDH formation at temperatures of 30 °C and 60 °C.

2. The phase composition and crystal structure of Zn-Al nitrate layered double hydroxide samples, obtained by syn-

thesis at a ratio of Zn:Al=4:1, a solution flow rate of 0.8 l/h,  $t=60$  °C, and pH=7, 8, 9, 10 have been studied. It has been shown that the samples synthesized at different pH are Zn-Al LDHs with the  $\alpha$ -Zn(OH)<sub>2</sub> crystal lattice of medium crystallinity, with an admixture of the oxide phase with the ZnO lattice. An increase in the pH of the synthesis leads to an increase in crystallinity.

3. The phase composition and crystal structure of Zn-Al nitrate layered double hydroxide samples, obtained by the synthesis method at a ratio of Zn:Al=4:1, pH=8,  $t=60$  °C, and solution flow rates of 0.8 and 1.6 l/hour have been studied. It has been shown that an increase in the solution flow rate does not change the phase composition and type of the crystal lattice of the samples. At the same time, with an increase in the solution flow rate, the crystallinity of the Zn-Al-nitrate LDH increases.

4. A retrospective comparative analysis of the phase composition and crystal structure of samples of Zn-Al-nitrate LDHs and Zn-Al LDHs intercalated with tripolyphosphate-, Tartrazine- and Orange Yellow S anions has been carried out (according to the data of previously published works). A significant effect of the nature of the anion on the phase composition and crystal structure of the samples has been revealed. It has been found that the use of large and multi-charged functional anions caused significant adsorption on precipitate nuclei and difficult intercalation. As a result, this leads either to the formation of a low-crystalline structure (for the Tartrazine-intercalated sample) or to the decomposition of a significant part of the LDH to an oxide component (tripolyphosphate- and Orange Yellow S-intercalated samples).

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