



УДК 546.185 : 543.422

INFLUENCE OF THE CATION NATURE ON SPECTRAL CHARACTERISTICS OF COBALT(II)-NICKEL(II) PHOSPHATES
ВПЛИВ ПРИРОДИ КАТІОНА НА СПЕКТРАЛЬНІ ХАРАКТЕРИСТИКИ КОБАЛЬТУ(II)-НІКОЛУ(II) ФОСФАТІВ

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Abstract. The work was carried out with the aim of studying the influence of the cation nature on the spectral characteristics of cobalt(II)-nickel(II) hydrogenphosphates of the general formula $Co_{1-x}Ni_xHPO_4 \cdot 1.5H_2O$ ($0 < x \leq 0.35$). Using the methods of Infrared and Raman spectroscopy, it was determined that in the structure of hydrogenphosphates there are two types of crystallographically non-identical water molecules that make up the coordination environment of cations. OH-groups of water molecules formed a hard system of different on strength and orientation of hydrogen bonds between molecules water and anion, also between the different OH-groups on the same molecule of water. The bond of OH-groups of phosphate tetrahedron is more labile. The influence of the cation nature on the asymmetry of the molecules of coordinated water, on the energy H-bonds, bonds $M^{II} - O(OH_2)$ and $P - OH$ were estimated. It was found that, impact of these bonds weaken with increasing content of nickel(II) in composition of the hydrogenphosphates. Asymmetry of water molecules also decreased, while the bonds $O - H$ coordinating water intensified with an increase a content of nickel(II) in composition of $Co_{1-x}Ni_xHPO_4 \cdot 1.5H_2O$. HOH angle formed independent OH-groups of the water molecules is not changes.

Key words: hydrogenphosphates, hydrogen bond, coordinated water, vibrational spectroscopy

Introduction.

In accordance with modern presentations, the molecules of water in the crystal lattice of crystallohydrates are involved in interactions with cationic and anionic undergrate of salt, determining the mechanism of their dehydration. Knowledge of it is necessary for choosing the conditions for obtaining anhydrous salts, which are uses to create functional materials for various branches of science and industry.

In hydrates of protonated phosphates, there are two types of H-bonds: involving protons of the hydrated anion and protons of water. Since the donor properties of protonated groups can vary widely, the interval of change in the value of the H-bond in these compounds is much larger than in average salts of the same cations. This determines the various properties of protonated phosphates and, first of all, the complication of their thermal dehydration reactions by the processes of water



dissociation and anionic condensation [1, 2]. Therefore, correct data on the state of water molecules contained in the structures of crystal hydrates are necessary for characterizing, substantiating, and predicting the complications of the dehydration processes of hydrated phosphates by solid-phase hydrolysis, the depth of which is also interconnected with the energy state of water molecules and proton-containing groups.

For individual phosphates of divalent metals, some data on the state of water molecules in their crystal structures are given in works [3-8]. Studies of the state of water in the structure of the cobalt (II) hydrogenphosphates was not performed. Only a few works are known, in which the spectral characteristics of $\text{CoHPO}_4 \cdot 1.5\text{H}_2\text{O}$ and its dehydration products are given [3, 8].

Data on the state of water in solid solutions of hydrated phosphates of divalent metals of different protonation and hydration is sparse [4,5,9]. Information on the systematic study of water state in the cobalt(II)-nickel(II) hydrogenphosphates in literature is absent.

The cobalt(II)-nickel(II) hydrogenphosphates were synthesized in the form of a limited solid solution of substitution of the general formula $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$, where $0 < x \leq 0.35$. They are formed as a result of isomorphic substitution of cobalt(II) for nickel(II) in the crystal lattice of $\text{CoHPO}_4 \cdot 1.5\text{H}_2\text{O}$, information about the structure of which is not available in the literature.

The hydrogenphosphates crystallize in the form of finely dispersed polycrystals, which complicates their X-ray structural analysis. Therefore, establishing the structural features of $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$, the nature of the relationship between various structural and functional groups in their crystal lattice, including the state of OH-groups, is possible only by indirect methods.

The methods of vibrational spectroscopy are the most informative for assessment of the OH groups of water molecules and protonated anion, their functional relation in the crystal lattice of crystalline hydrates [10].

The aim of this work – by means of Infrared and Raman spectroscopy to investigate the state of water in the cobalt(II)-nickel(II) hydrogenphosphates and to evaluate the influence of the nature of the cation on it.

Experimental.

As objects researches used the cobalt(II)-nickel(II) hydrogenphosphates of composition $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.35$) with different content of cobalt(II) and nickel(II): $\text{Co}_{0,9}\text{Ni}_{0,1}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$, $\text{Co}_{0,8}\text{Ni}_{0,2}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$, $\text{Co}_{0,7}\text{Ni}_{0,3}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ and $\text{Co}_{0,65}\text{Ni}_{0,35}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$. These samples were prepared by reacting of phosphoric acid (64.13 wt % P_2O_5) with a mechanical mixture of hydroxocarbonates at a fixed pH value within 2.2-2.4, similar to [11].

IR spectrums were recorded at 20°C and -190°C in the range of 400-4000 cm^{-1} on a spectrometers Specord 75 IR and Nexus - 470 with Fourier transformation and Omnic softwares. The samples were prepared by pressing of the fixed amount (0,05 mas.%) in the matrix of KBr. In addition, the suspension of hydrogenphosphates in a butyl alcohol, inflicted on a neutral fluorite substrate were used. For the improvement of stripes resolution and reduction of general background vaseline oil added in a suspension. The Raman spectrums registered on the spectrometer of DFS-24 (a source of excitation is an argon laser, $\lambda_0 = 514.5 \text{ nm}$).



In order to correctly assign the absorption bands caused by the fluctuations of proton-containing groups, a comparative analysis of the IR and Raman spectrums of the investigated solid solutions of phosphates and their deuteroanalogs, recorded at room temperature (20°C) and when the sample is cooled to a temperature of -190 °C, is carried out.

Results and discussion.

According to the obtained data, in the IR spectrums of hydrogenphosphates of solid solution of $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ different of composition, recorded at 20°C, in the region of valence vibrations of OH-groups (3000-3600 cm^{-1}) are observed two absorption bands and deformation vibrations of water molecules (1550-1750 cm^{-1}) are observed two absorption bands. In the range of 1900-2800 cm^{-1} , a set of absorption bands characteristic of bands of type A, B and C are recorded. These bands are characteristic of the spectra of salts containing protonated anions. In the region of skeletal vibrations of the anion (400-1400 cm^{-1}) there are two separate bands at 1360 and 880 cm^{-1} and three groups of absorption bands in the ranges of 1080-980 cm^{-1} , 750-720 cm^{-1} and 580-510 cm^{-1} (Figure 1).

In the Raman spectra of hydrogenphosphates Co(II)- Ni(II) in the area of $\nu(\text{OH})$ molecules of the crystallization water, a wide band 2800-3600 cm^{-1} is recorded; in the range $\delta(\text{H}_2\text{O})$ – the peak of low intensity with a maximum of 1640-1645 cm^{-1} . Four bands in the region 850-1100 cm^{-1} correspond to vibrations of the phosphate anion.

The decline of temperature does not make a fundamental difference in the nature of the hydrogenphosphates Co(II)- Ni(II) spectral curves (Figure 1). In area of vibrations $\nu(\text{OH})$ and $\delta(\text{H}_2\text{O})$ in IR spectra, which were recorded at -190°C are observed two stripes of absorption, intensity of that increases in comparing to the analogical stripes in the spectra obtained at 20°C. Stripes of type A, B, C at -190°C become more contrast, their intensity increases; stripe A registers at 2900 cm^{-1} .

The decrease of the temperature in the range of fluctuations of phosphate anion led to a redistribution of the intensities of the bands 1360, 1040 cm^{-1} bands and groups of 750-720 cm^{-1} , 580-510 cm^{-1} in the direction of increasing the intensity of low-frequency lines. According to the spectral position of the maxima of these absorption bands and the sensitivity to temperature changes of the bands associated with the vibrations of groups containing protons, they can be correlated with the following vibrations: protonated anion: deformation planar $\delta(\text{POH})$ – 1360 cm^{-1} , the low-frequency component of asymmetric valence vibrations ν_{as} – 1040 cm^{-1} , deformation out-of-plane $\gamma(\text{POH})$ – 750, 720 cm^{-1} and symmetric deformation vibrations $\delta(\text{O}_3\text{PO})$ – 580, 530, 510 cm^{-1} .

The interpretation of infrared and Raman spectra showed that in the structure of hydrogenphosphates $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ there are two types of crystallographic unidentical water molecules, which are included in coordinating surroundings of cation. Two stripes $\delta(\text{H}_2\text{O})$ indicate on it (1630 and 1580 cm^{-1}). Their presence in the IR spectrum, according to [1,10], is a identification sign of the presence in the crystalhydrate of water molecule as of structural unit. This is evidenced by the difference in the values of the maxima of bands $\nu(\text{OH})$ in the spectra of Co(II)-Ni(II) hydrogenphosphates, which is 200-240 cm^{-1} .

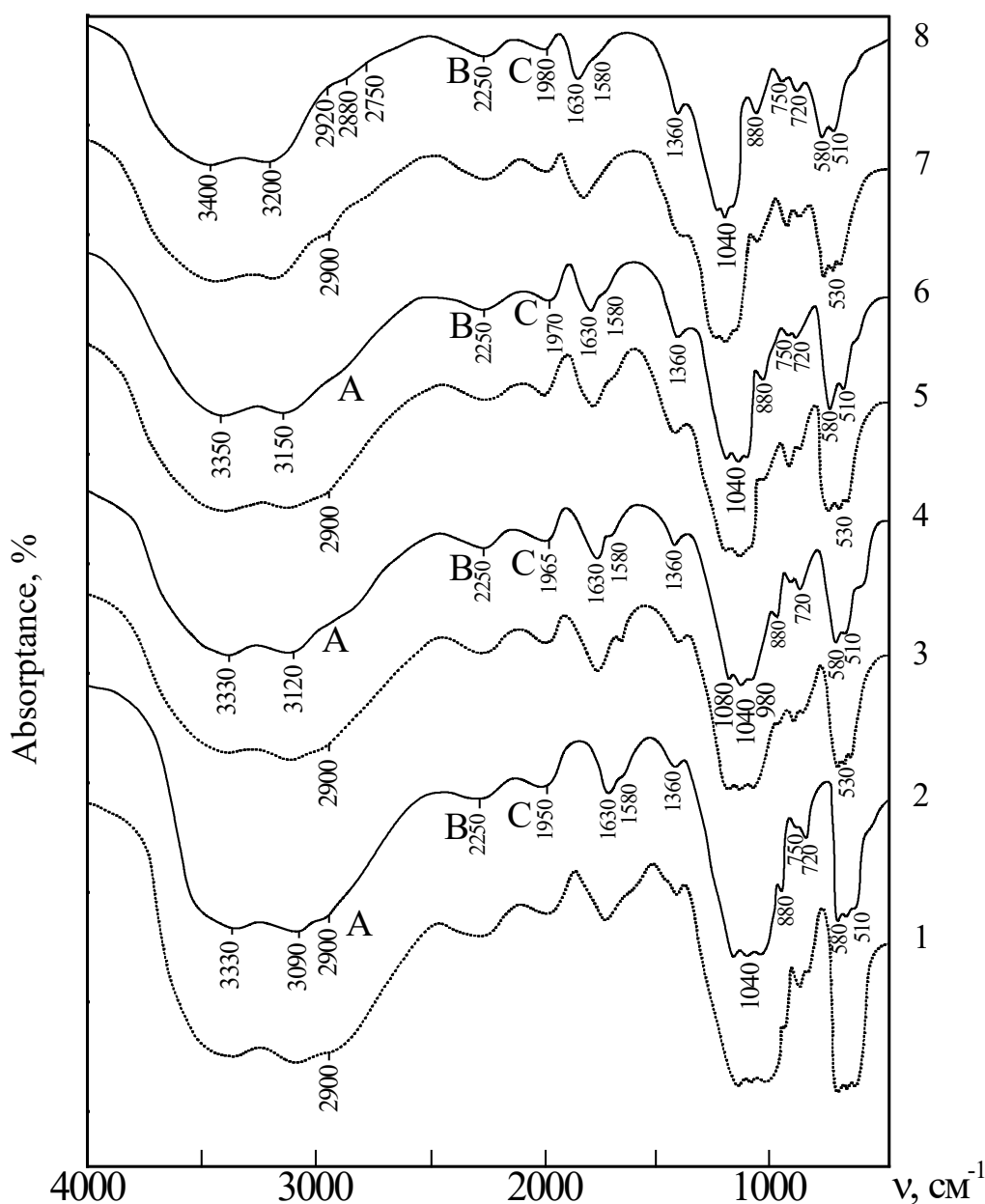


Figure 1 – IR spectra of absorption of $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ with $x = 0$ (1,2), 0.1 (3,4), 0.3 (5,6), 0.35 (7,8), recorded at 20°C (2, 4, 6, 8) and -190°C (1, 3, 5, 7)

The value of $\Delta\nu$ for $\text{Co}_{0.9}\text{Ni}_{0.1}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$, for example, is 210 cm^{-1} and is decreased to 200 cm^{-1} in IR spectrum of hydrogenphosphate with maximal content of nickel(II) – $\text{Co}_{0.65}\text{Ni}_{0.35}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ (Figure 1). It allows to consider fluctuations each of the two OH-groups of the same water molecule as independent of each other and to consider that they are involved in the formation of different strength and directivity of H-bonds. Thus, HOH angle in water molecules does not depend on the composition of hydrogenphosphates. Practically identical values of $\delta(\text{H}_2\text{O})$ maximums indicate this. The absence of significant changes in the $\delta(\text{H}_2\text{O})$ in the spectra recorded at -190°C , and large values of their frequency (1630 cm^{-1} comparing to frequency of vibrations of free molecule of water – 1595 cm^{-1}) indicate the existence in the structure of $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ hard system of hydrogen bonds.



The comparative analysis of the IR spectrums of $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ with various composition made it possible to distinguish two conventional spectral regions on the absorption curves. One of them is the range of $4000\text{-}1900\text{ cm}^{-1}$, in which the influence of the cation nature on the state of OH-groups is quite significant. This area is typical of the stretching vibrations of the OH-groups of water molecules and the frequency components caused by fluctuations of the P – OH bonds of protonated anions, which form strong hydrogen bonds. The second range – $1900\text{-}400\text{ cm}^{-1}$, in which changes in the spectra are not obvious. The same pattern of change in the shape of the spectral curve persists at low temperature survey (Figure 1).

In area of $\nu(\text{OH})$ of cationic sublattice two stripes are fixed, the spectral position of maxima of which varied depending on the composition of hydrogenphosphates. Thus the frequency of 3330 cm^{-1} characteristic $\text{CoHPO}_4 \cdot 1.5\text{H}_2\text{O}$ [8], remains unchanged and in IR spectrum of $\text{Co}_{0.9}\text{Ni}_{0.1}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$. The maximum of this band is shifted to 3350 cm^{-1} by further increasing the nickel(II) content in the composition $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ (up to $x = 0.3$). The shift reached its maximum value (70 cm^{-1}) in the IR spectrum of hydrogenphosphate, the composition of which corresponds to the saturated solid solution – $\text{Co}_{0.65}\text{Ni}_{0.35}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ (Figure 1).

The changes in the value of the maximum of the second absorption band (from 3090 cm^{-1} to 3120 cm^{-1}), which is characterizes fluctuations in the OH-groups, involved in the formation of stronger hydrogen bonds, are records even in the IR spectrum of hydrogenphosphate, which consist of minimal content of nickel(II) – $\text{Co}_{0.9}\text{Ni}_{0.1}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$. Maximum shift value (110 cm^{-1}) of this band also was gained in the infrared spectrum $\text{Co}_{0.65}\text{Ni}_{0.35}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$.

Most clearly the influence of the second cation in the state of OH-groups in the crystal lattice $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ registers in IR spectra hydrogenphosphates inflicted on fluorite substrate (Figure 2).

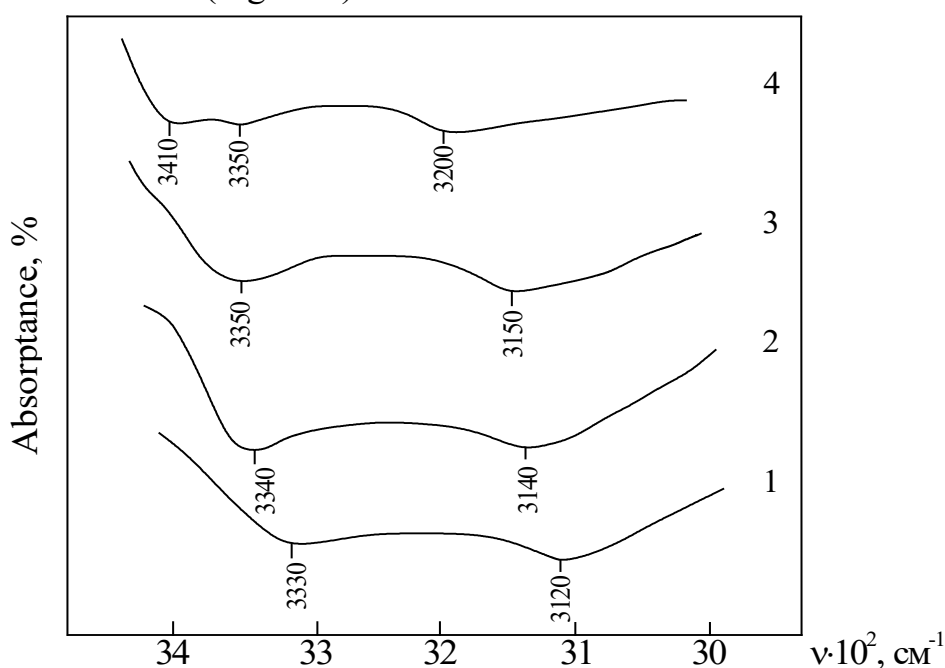


Figure 2 – IR spectrums of absorption of $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ (20°C) with $x = 0.1$ (1), 0.2 (2), 0.3 (3), 0.35 (4), were inflicted on a substrate from CaF_2 .



In the spectrum of hydrogenphosphate with maximal content of nickel ($x = 0.35$), except for displacement $\nu(\text{OH})$ in a high-frequency range, is fixed splitting of the main absorption band (3400 cm^{-1}) on two frequencies – 3410 and 3350 cm^{-1} . The changes in the IR spectrums of hydrogenphosphates, that are observed increasing content of nickel(II) in their composition, characterize attenuation in the structure of $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ entire system of H-bonds. There are bonds between OH-groups of water and anion, and between different OH-groups on the same molecule of water.

For the estimation the influence of cation nature on OH-groups protonated anion (P–OH) the comparative analysis of position in IR spectrums of $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ of stripes of type A, B and C was performed. The changes in the group of absorption bands in the infrared spectra of hydrogenphosphates with different content of nickel(II) were observed only for C band. The maximum of this band (1950 cm^{-1} for $\text{CoHPO}_4 \cdot 1.5\text{H}_2\text{O}$) shifted the high-frequency region of spectrum (to 1980 cm^{-1} for hydrogenphosphate with $x = 0.35$) with simultaneous reduction to intensity. Such character of changes indicate that phosphatic anions along with the water molecules were included in coordinating surroundings of cation. Consequently, changes of bond length of cation-ligand and degree of ionicity in $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ were observed in IR spectrums. In case of substitution of cobalt to nickel(II) these bonds weakened. This leads to a shift of the absorption maximum and intensity change of absorption band, which correlated with fluctuations of the protonated anion (Figure 1).

In the second conditionally distinguished spectral interval, displacement maxima of absorption bands that characterize bonds OH-groups are virtually absent. The influence of cation nature was appeared only in the redistribution of intensities of individual lines. The most sensitive to the changes in cationic undergrate was the low-frequency component of asymmetric valence vibration of anion with a maximum of 1040 cm^{-1} (Figure1). With an increase a content of nickel(II) in the composition of $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ intensity of this stripe of absorption increases. It is, respectively [1,10], by evidence of reduction of durability of bond, in this case of bond P – OH.

Conclusions.

The state of water in cobalt(II)-nickel(II) hydrogenphosphates with the general formula $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.35$) using the methods of vibrational spectroscopy was investigated. The influence of the cation nature on it was evaluated.

It was determined that there are two types of crystallographic non-identical water molecules that constitute the coordination surrounding of the cations in the structure of hydrogenphosphates $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.35$). These OH-groups of water molecules formed a hard system of different on strength and orientation of hydrogen bonds between molecules water and anion, also between the different OH-groups on the same molecule of water.

The bond of OH-groups of phosphate tetrahedron is more labile. The influence of the cation nature on the asymmetry of the molecules of coordinated water, on the energy H-bonds, bonds $\text{M}^{\text{II}} - \text{O} (\text{OH}_2)$ and P – OH were estimated. It was found that, impact of these bonds weaken with increasing content of nickel(II) in composition of the hydrogenphosphates.

Asymmetry of water molecules also decreased, while the bonds O – H coordinating water intensified with an increase a content of nickel(II) in composition



of $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$. HOH angle formed independent OH-groups of the water molecules is not changes.

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Анотація. Роботу виконано з метою дослідження впливу природи катіона на спектральні характеристики кобальту(II)-ніколу(II) гідрогенфосфатів загальної формули $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.35$) різного катіонного складу. Методами інфрачервоної та комбінаційної спектроскопії визначено, що в структурі гідрогенфосфатів існують два типи кристалографічно неідентичних молекул води, які складають координаційне оточення катіонів. OH-групи молекул води утворюють жорстку систему різних за міцністю і напрямленістю Н-зв'язків. Зв'язок OH-груп фосфатного тетраедра більш лабільний. Оцінено вплив природи катіонів на асиметрію молекул координованої води, на енергію Н-зв'язків, зв'язків $\text{M}^{\text{II}} - \text{O}(\text{OH}_2)$ та $\text{P} - \text{OH}$. Встановлено, що вплив цих зв'язків слабшає зі збільшенням вмісту ніколу(II) у складі гідрогенфосфатів. Зменшується також асиметрія молекул води, а зв'язки $\text{O} - \text{H}$ координованої води посилюються зі збільшенням вмісту ніколу(II) у складі $\text{Co}_{1-x}\text{Ni}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.35$). Кут НОН, утворений незалежними OH-групами молекул води, не змінюється

Ключові слова: гідрогенфосфати, спектральні характеристики, водневі зв'язки, природа катіона.

Стаття відправлена: 30.07.2023 р.

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