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Electronic structure and atomic structure peculiarities of isomorphic modified zinc diphosphates

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Effects of partial substitution of Zn by Mn on the electronic and atomic structure of diphosphates $Zn_{2-x}Mn_xP_2O_7{\cdot}5H_2O$ (x = 0.0, 0.7) have been studied out by X-ray photoelectron spectroscopy, IR spectroscopy, NMR and thermogravimetric analysis. Analysis of the infrared absorption spectra was carried out for functional groups of $Zn_2P_2O_7{\cdot}5H_2O$ and $Zn_{1.3}Mn_{0.7}P_2O_7{\cdot}5H_2O$ compounds. Through correlation between the symmetric and asymmetric stretching vibrations of P–O–P bridge and P–O–P angle an increase of P–O–P bridge angle was established for $Zn_{1.3}Mn_{0.7}P_2O_7.5H_2O$. Substitution of zinc by manganese has little impact on the overall balance of chemical bond in the compound, which is manifested in minor changes of the core electrons binding energies.

Методами рентгеновской фотоэлектронной спектроскопии, ИК и ЯМР спектроскопии и термогравиметрического анализа исследовано влияние частичного замещения цинка марганцем на электронное строение и структурные параметры дифосфатов $Zn_{2-x}Mn_xP_2O_7{\cdot}5H_2O$ (x = 0.0, 0.7). Проведен анализ ИК-полос поглощения, характеризующих колебания функциональных групп соединений $Zn_2P_2O_7{\cdot}5H_2O$ и $Zn_{1.3}Mn_{0.7}P_2O_7{\cdot}5H_2O$. Исходя из корреляций симметричных и асимметричных валентных колебаний мостиковой связи P–O–P, установлено увеличение угла P–O–P в соединении $Zn_{1.3}Mn_{0.7}P_2O_7{\cdot}5H_2O$. Замещение цинка марганцем мало нарушает общий баланс химической связи в соединении, проявляющейся в незначительных изменениях энергий связи остовных уровней компонент.

Електронна будова і структурні особливості атомів ізоморфномодифікованого дифосфату цинку. *С.С.Смоляк, В.Л.Карбівський, В.Х.Касіяненко.*
За допомогою рентгенівської фотоелектронної спектроскопії, ІЧ і ЯМР спіктроскопії та термогравіметричного аналізу вивчено вплив ізоморфного заміщення цинку марганцем на електронну будову та структурні параметри дифосфатів $Zn_{2-x}Mn_xP_2O_7{\cdot}5H_2O$ (x = 0.0, 0.7). Проведено аналіз ІЧ-смуг поглинання, що характеризують коливання функціональних груп сполук $Zn_2P_2O_7{\cdot}5H_2O$ і $Zn_{1.3}Mn_{0.7}P_2O_7{\cdot}5H_2O$. Виходячи з кореляцій симетричних і асиметричних валентних коливань місткового зв'язку P–O–P, встановлено збільшення кута P–O–P у сполуці $Zn_{1.3}Mn_{0.7}P_2O_7{\cdot}5H_2O$. Заміщення цинку марганцем мало порушує загальний баланс хімічного зв'язку у сполуці, що виявляється в незначних змінах енергій зв'язку остовних рівнів компонент.

1. Introduction

Currently, there is a growing interest in development of the new inorganic materials for practical applications. A wide range of industrial applications have phosphate materials, for example, diphosphates of lithium and polyvalent metals recently started to be used as electrode materials in autono-

mous power sources [1–4]. No less interesting and promising for usage as electrode materials are diphosphates containing lithium and polyvalent metals in the lower oxidation states. For example $LiM_{III}P_2O_7$ or $Li_3M_{III2}(PO_4)_3$ (M_{III} — Fe, V, Ti, Mo) [5].

Earlier it was studied the structural features of $Mn_{2-x}Co_xP_2O_7{\cdot}5H_2O$, which are promising materials for their use as pigments, catalysts and environmentally friendly corrosion inhibitors [6, 7]. Electronic structure of these compounds was investigated in [8]. Their electronic structure peculiarities were studied by us in [8]. The structural characteristics and thermal properties of diphosphates $Zn_2P_2O_7{\cdot}5H_2O$ were reported in [9, 10]. The results of spectral-luminescent and vibrational properties are presented in [11]. However, information about the electronic structure of $Zn_2P_2O_7{\cdot}5H_2O$ is absent for now.

In this context, the aim of this work is to study the electronic structure features and structural characteristics of diphosphates $Zn_2P_2O_7{\cdot}5H_2O$ and $Zn_{1.3}Mn_{0.7}P_2O_7{\cdot}5H_2O$.

2. Experimental

In the current work methods of X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR) and thermogravimetry were used.

X-ray photoelectron spectra of the samples — $Zn_{1.3}Mn_{0.7}P_2O_7{\cdot}5H_2O$ and $Zn_2P_2O_7{\cdot}5H_2O$ were obtained by a photoelectron spectrometer of "JEOL" company — "JSPM-4610" with using of non-monochromatic Mg K_α (1253.6 eV) X-ray source. Calibration of X-ray photoelectron spectra was carried out using the binding energy of gold Au 4*f* lines, thus providing to obtain a sufficiently high determination accuracy of the electron binding energies for the samples elements. During the experiment, pressure in an analytical chamber was 10^{-7} Pa, the accuracy of the binding energy determination was 0.1 eV. The samples were prepared as disperse powder deposited on the aluminium substrate.

NMR spectra were recorded on a "Bruker" Avance 400 spectrometer at the room temperature.

To obtain IR spectra, the samples were shaped as tablets. The transmission spectra were recorded in absorption band of P_2O_7 anion from 1300 cm^{-1} to 400 cm^{-1} using dual-beam spectrophotometer "Specord M80" (recording range 4000–250 cm^{-1}).

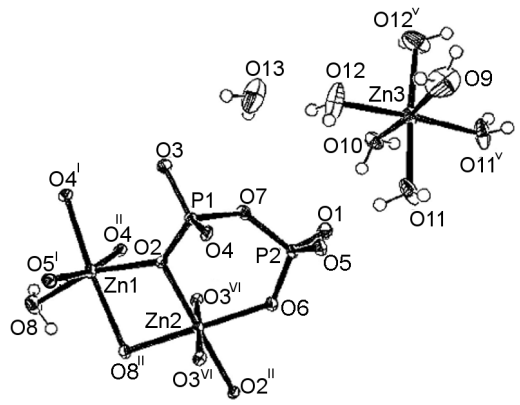

Fig. 1. Structure of $Zn_4(P_2O_7)_2{\cdot}10H_2O$ [9].

Thermograms were recorded by Q-1500D derivatograph of MOM company. The samples with mass ~40–50 mg were studied in thermogravimetric platinum crucibles at temperature ranging from the room temperature up to 1000°C at a heating rate of 5°C/min, in air (limited area), at the free convection exchange.

3. Results and discussion

It is known [9] that $Zn_2P_2O_7{\cdot}5H_2O$ crystallizes in orthorhombic symmetry with the space group P_{nma} (D_{2h}^{16}). In structure of $Zn_2P_2O_7{\cdot}5H_2O$ there are present two crystallographically nonequivalent atoms of phosphorus forming groups P_2O_7, and three nonequivalent atoms of the metal. $Zn_2P_2O_7{\cdot}5H_2O$ consists of packed layers of ZnO_6 octahedra, connected by double tetrahedral P_2O_7-groups — $[Zn_3O_2(H_2P_2O_7)_2{\cdot}2H_2O]$ and layers of $[Zn(3)(H_2O)_6]$ groups (Fig. 1). $P_2O_7^{4-}$ anions have nonlinear configuration with P–O–P bridging angle equal to 126.5° [6, 9].

To assess the changes in the atomic structure of diphosphates $Zn_{2-x}Mn_xP_2O_7{\cdot}5H_2O$ (x = 0.0, 0.7) infrared spectra were obtained (Fig. 2). IR spectra consist of different bands corresponding to the vibrations of water molecules, PO_3 groups and P–O–P bridge. The assignment of frequencies for the both samples is given in Table 1. Position of the bands is consistent with the previous results [9], however, the number of observed vibrational modes does not correspond to the quantity provided by the compound symmetry. Apparently, this is due to the overlap of some bands or due to insufficient intensity of the individual modes [9]. Less number of the vibrational modes was also observed for α–$Zn_2P_2O_7$, α-, β–$Mg_2P_2O_7$ and

Table 1. Vibrational band assignments for $Zn_{2-x}Mn_xP_2O_7 \cdot 5H_2O$ (cm^{-1})

Position of vibrational bands for $Zn_{2-x}Mn_xP_2O_7 \cdot 5H_2O$ (cm^{-1})		Assignment
x = 0.0	x = 0.7	
3712	3712	νH_2O
1648	1648	δH_2O
1144	1144	$\nu_s PO_3$
1088	1080	+
	1040	$\nu_{as} PO_3$
912	912	ν_{as}POP
744	736	ν_sPOP
672		ρH_2O
560	552	$\delta_{as} PO_3$
488	480	

$Ca_2P_2O_7$, as expected according to the group of symmetry [9].

For the sample $Zn_2P_2O_7 \cdot 5H_2O$ there are two modes — 1144 cm^{-1} and 1080 cm^{-1} in the area of symmetric and asymmetric stretching vibrations of PO_3-groups. For the sample of diphosphate $Zn_{2-x}Mn_xP_2O_7 \cdot 5H_2O$ where $x = 0.7$, the number of vibrational modes increases to three — 1144 cm^{-1}, 1080 cm^{-1} and 1040 cm^{-1} (Fig. 2, Table 1).

Two absorption bands — 766 cm^{-1} (ν_s) and 929 cm^{-1} (ν_{as}) correspond to the stretching vibrations of P–O–P bridge. The presence of these two modes in the spectrum indicates that the angle POP < 180° and that the symmetry of P_2O_7-group cannot be higher than C_{2v}, because only one mode vas can be observed for centrosymmetric (angle POP = 180°) configuration (symmetry group D_{3d}).

In the frequency range of 2500 cm^{-1}–3700 cm^{-1} there are observed the broad overlapping absorption bands corresponding to stretching vibrations of water molecules νH_2O, that can be explained by formation of various hydrogen bonds. This assumption is confirmed by the authors of [6, 9] for the analogous compounds. Deformation modes

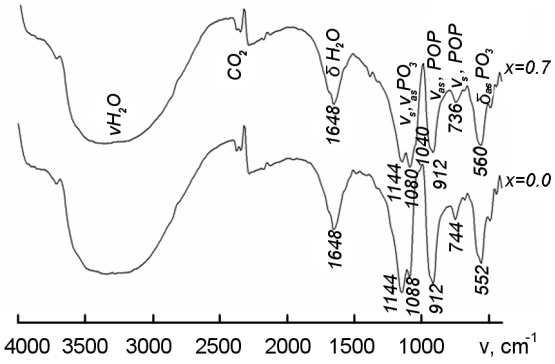

Fig. 2. IR absorption spectra of diphosphates $Zn_{2-x}Mn_xP_2O_7 \cdot 5H_2O$, where x = 0.0, 0.7.

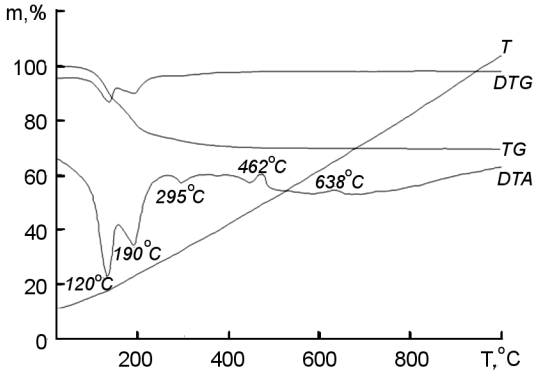

Fig. 3. DTA, TG and DTG curves of $Zn_2P_2O_7 \cdot 5H_2O$.

of water molecules for the both samples are observed in the area of 1648 cm^{-1}.

Position of observed vibrational modes ν_s and ν_{as} can be used for the experimental determination of the POP angle in these compounds. To estimate the magnitude of the POP angle we used the relationship between the angle and the magnitude of splitting of P_2O_7-group vibrations proposed by Lazarev: $\Delta = [\nu_{as} - \nu_s POP]/[\nu_{as} + \nu_s POP]$ [12]. Experimentally obtained dependence of this quantity Δ against the POP angle of P_2O_7-group is given in [13]. The values of POP angle for studied compounds obtained on the basis of these data are shown in Table 2.

Table 2. Values of 100·Δ and POP angle for the samples of $Zn_{2-x}Mn_xP_2O_7 \cdot 5H_2O$ (x = 0.0, 0.7)

	ν_{as}POP, (IR, cm^{-1})	ν_sPOP, (IR, cm^{-1})	100·Δ	Angle POP, deg., according to [13]
$Zn_2P_2O_7 \cdot 5H_2O$	912	744	10.14	125
$Zn_{1.3}Mn_{0.7}P_2O_7 \cdot 5H_2O$	912	736	10.68	127

Parameter 100·Δ for $Zn_2P_2O_7·5H_2O$ is 10.14 that corresponds to angle of 125°, and practically coincides with the value obtained in [9], where the angle was determined as 126.5°. For compound $Zn_{1.3}Mn_{0.7}P_2O_7·5H_2O$ the parameter 100·Δ is 10.68, that corresponds to the angle POP equal to 127°.

The nature of thermal processes in the temperature range from ≈20°C to 1000°C for diphosphates $Zn_{2-x}Mn_xP_2O_7·5H_2O$ (x = 0.0, 0.7) can be seen from the curves of DTA, TG and DTG (Fig. 3, Fig 4).

Thus on the DTA curve for $Zn_2P_2O_7·5H_2O$ (Fig. 3, Table 3) there are two deep minima at 120°C and 190°C and weak minimum at 295°C corresponding to endoeffects. These effects are caused by the mass loss — removal of water molecules at different stages. The DTG curve indicates that the processes of mass loss proceed in three stages. Exoeffects at 462°C and 638°C are not accompanied by loss of mass and probably is due to crystallization of intermediary products. This is consistent with the results obtained in [9] for compound $Zn_2P_2O_7·5H_2O$, where at 295°C the amorphous $Zn_2P_2O_7$ was observed, at 481°C the crystallization of γ–$Zn_2P_2O_7$ took place and at 750°C the transformation of the γ-phase in β–$Zn_2P_2O_7$ occurred. The transition between the γ–$Zn_2P_2O_7$ and β–$Zn_2P_2O_7$ is irreversible, but cooling of β–$Zn_2P_2O_7$ to the room temperature leads to formation of α—$Zn_2P_2O_7$ [9].

Presence in the sample of $Zn_{2-x}Mn_xP_2O_7·5H_2O$ two types of cations (x = 0.7) (Fig. 4, Table 3) reduces the thermal stability — the weaker bonds of water molecules broken at 82.5°C (see the curve DTG). This is evidenced by the endotherm

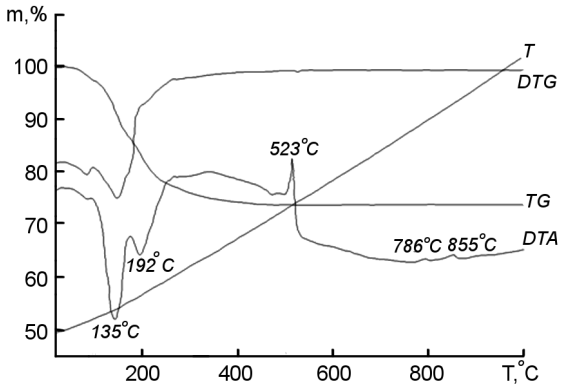

Fig. 4. DTA, TG and DTG curves of $Zn_{2-x}Mn_xP_2O_7·5H_2O$, x = 0.7.

effect on the DTA curve at this temperature. The deep endoeffect with a minimum at 135°C is accompanied by a significant loss of mass and the highest rate of the mass loss. The less intensive endoeffect at 192°C is characterized by the minor loss of mass. There is also a low-intensity endoeffect at 270°C. The DTG curve confirms the jagged mass loss model. Unlike $Zn_2P_2O_7·5H_2O$, for compound $Zn_{1.3}Mn_{0.7}P_2O_7·5H_2O$ three exoeffects at temperatures 523°C, 786°C and 855°C are observed, which are associated with transformations of the heated material without the loss of mass.

Infrared spectroscopy is very informative method for studying the heating products, because of removal of functional groups during the heating of the substance reduces or totally eliminates the intensity of the corresponding absorption band. Heating of the test compounds (up to 1000°C) leads to a loss of water molecules. (?) — IR spectra of the samples have no vibrational modes corresponding to the water molecules (this area is not presented here). IR spectra of the heating products of the studied com-

Table 3. Peak positions of the thermal effects (°C) for $Zn_{2-x}Mn_xP_2O_7·5H_2O$

	Energy effects, accompanied by mass loss				Energy effects without massloss	Mass loss, wt. %
	t, °C					
x	Endo	Endo	Endo	Endo	Exo	
0.0	120.0	190	295*	450*	462 638*	22.7
0.7	82.5 135	192	270*		523 786* 855*	26.2

Note: * — weak intensity.

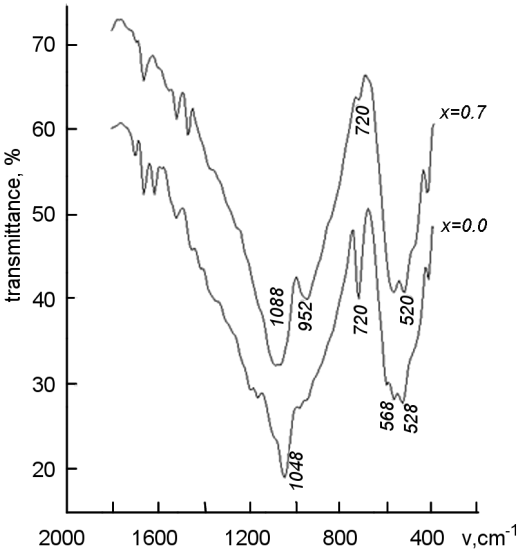

Fig. 5. IR absorption spectra of diphosphates $Zn_{2-x}Mn_xP_2O_7{\cdot}5H_2O$ (x = 0.0, 0.7), heated up to 1000°C.

pounds (see Fig. 5) have vibration modes corresponding to ν_sPOP, that indicates the curved shape of the POP bridge. Shift of the vibrational modes ν_sPOP after heating is observed for the both samples to the lower frequencies on 16 cm^{-1} and 24 cm^{-1} with respect to the samples in the initial state. A significant shift towards the higher frequencies is observed for ν_{as}POP mode. According to [12], decrease of ν_sPOP frequency and increase of ν_{as}POP frequency indicates the increase of POP angle. Spectroscopic evaluation of the angle for the heating products of these compounds shows that in the case of $Zn_2P_2O_7{\cdot}5H_2O$ the final product has POP angle equal to ~140°. It is assumed that the heating of this compound led to the formation of α–$Zn_2P_2O_7$ phase, because it is known from [9] that heating of $Zn_2P_2O_7{\cdot}5H_2O$ results in formation of α–$Zn_2P_2O_7$ with POP angle equal to 139°. IR spectrum of the heating product of $Zn_{2-x}Mn_xP_2O_7{\cdot}5H_2O$, x = 0.7 is more blurred, ν_sPOP mode has low-intensity and POP angle is about 148°.

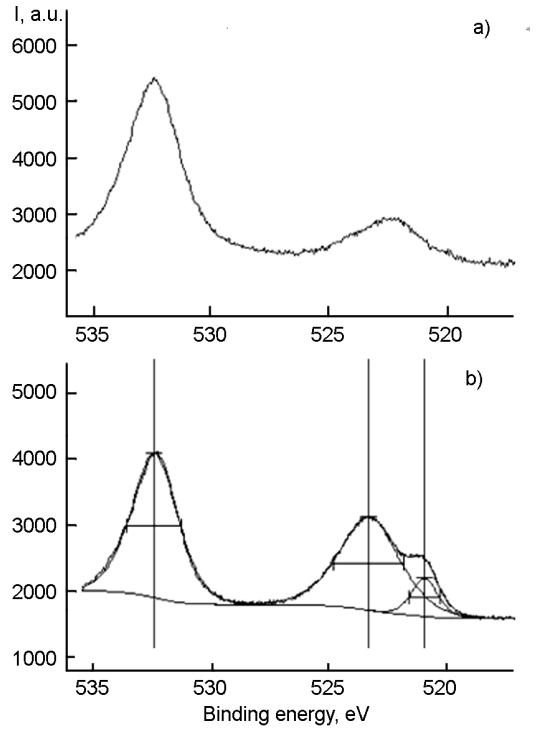

Fig. 6. O 1s XPS spectra for $Zn_2P_2O_7{\cdot}5H_2O$ (a) and $Zn_{1.3}Mn_{0.7}P_2O_7{\cdot}5H_2O$ (b).

From comparison of the thermal effects temperatures for $Zn_{2-x}Mn_xP_2O_7{\cdot}5H_2O$, x = 0.0, 0.7 it is seen that the sample with the value of x = 0.0 is more resistant to the thermal stresses.

Electronic structure of the investigated compounds was studied by X-ray photoelectron spectroscopy. Fig. 6 shows the XPS spectra of 1s states of oxygen, which are characterized by approximately the same parameters. One can see that their energy position, width and asymmetry parameter are almost matching. As can be seen from Table 4, the partial substitution of zinc by manganese is accompanied by some increase in the energy of 2p core electrons of zinc by 0.2 eV. Such small changes in the positions of the core electrons spectra indicate the spatial redistribution of the electron density while maintaining the overall energy balance of the chemical bond.

Participation in the bond of 3d-orbitals of manganese results in significant broaden-

Table 4. Binding energy (eV) of the core levels of atoms for the studied compounds

	O1s	Zn2$p_{3/2}$	Zn2$p_{1/2}$	Mn2$p_{3/2}$	Mn2$p_{1/2}$
$Zn_2P_2O_7{\cdot}5H_2O$	532.5	1023.4	1046.5	–	–
$Zn_{1.3}Mn_{0.7}P_2O_7{\cdot}5H_2O$	532.5	1023.5	1046.7	642.8	654.5

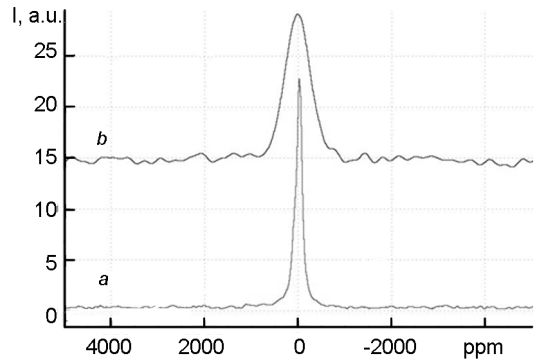

Fig. 7. ^{31}P NMR spectra of compounds: a) — $Zn_2P_2O_7 \cdot 5H_2O$; b) — $Zn_{1.3}Mn_{0.7}P_2O_7 \cdot 5H_2O$.

ing of the nuclear magnetic resonance spectra obtained on the nuclei of phosphorus ^{31}P (Fig. 7). This broadening is caused by the presence of magnetic moment on manganese atoms due to the existence of its unpaired electrons on 3*d*-orbitals, that leads to the broadening of ^{31}P NMR line.

4. Conclusions

For zinc diphosphate the value of P–O–P bridge angle was determined, which is equal to 125°. Isomorphic substitution of zinc by manganese — $Zn_{1.3}Mn_{0.7}P_2O_7 \cdot 5H_2O$ leads to a slight increase in the P–O–P bond angle, which amount to 127°.

Annealing of the samples of $Zn_2P_2O_7 \cdot 5H_2O$ and isomorphically substituted $Zn_{1.3}Mn_{0.7}P_2O_7 \cdot 5H_2O$ at 1000°C leads to the phase transformations and to significant increase in the angles of P–O–P bond, which are equal to 139° and 148°, respectively.

Loss of structural water for $Zn_2P_2O_7 \cdot 5H_2O$ compound take place at the higher temperatures, that indicates the presence of stronger hydrogen bonds and more stable structure of this compound. Doping of zinc diphosphate reduces the thermal stability of the compound. The weaker bonds of water molecules break even at 82.5°C.

Isomorphic doping of zinc diphosphate by manganese has little impact on the overall balance of the chemical bond in the compound, which is manifested in minor changes of the core electrons binding energies.

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