

Double phosphates $\text{NaMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ and $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ — advanced functional materials

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Complex phosphates containing two different ions have been identified in the fluxes of $\text{M}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3$ systems (where M — Na, K) for the first time. Optimum conditions for the growing of single crystals of $\text{NaMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ and $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ compounds have been selected. Complete X-ray diffraction analysis has been performed to study single crystals of synthesized phosphates $\text{MMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ (where M — Na, K). The structure of compounds is defined by the monoclinic crystal system (space group $P2_1/m$) with lattice parameters: $a = 5.350$ (5.358) Å, $b = 26.643$ (26.697) Å, $c = 6.566$ (6.575) Å, $\beta = 107.25^\circ$ (107.22°); $Z = 2$, $\rho = 3.575$ (3.568) g/cm³, respectively. The synthesized compounds have been studied using the following techniques: DTA, IR- and EPR-spectroscopy, magnetochemistry; the dependence of dielectric constant on the temperature has been measured for the obtained phosphates. Slight antiferromagnetic interaction has been detected in octahedron chains $[\text{MnO}_6]$. Based on the findings from conducted research, a set of physicochemical properties has been proposed for the synthesized compounds, which can be utilized in the development of these functional materials.

Keywords: complex phosphates, EPR, flux crystallization, XRD.

Впервые в расплавах систем $\text{M}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3$ (где M — Na, K) выделены сложные фосфаты, содержащие два разных иона. Подобраны оптимальные условия для выращивания монокристаллов соединений $\text{NaMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ и $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$. Проведено рентгеноструктурное исследование монокристаллов синтезированных фосфатов $\text{MMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ (где M — Na, K). Структура соединений относится к моноклинной сингонии (пр. гр. $P2_1/m$), параметры решетки равны: $a = 5.350$ (5.358) Å, $b = 26.643$ (26.697) Å, $c = 6.566$ (6.575) Å, $\beta = 107.25^\circ$ (107.22°); $Z = 2$, $\rho = 3.575$ (3.568) г/см³ соответственно. Синтезированные соединения исследованы методами ДТА, ЭПР-спектроскопии, магнетохимии, измерены зависимости диэлектрической постоянной от температуры. Установлено наличие слабого антиферромагнитного взаимодействия в цепочках октаэдров $[\text{MnO}_6]$. В результате проведенных исследований предложен ряд физико-химических характеристик синтезированных соединений, которые можно использовать в разработке данных функциональных материалов.

Подвійні фосфати $\text{NaMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ та $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ — перспективні функціональні матеріали. *П.Г.Нагорний, М.С.Слободяник, Т.І.Ущяпівська, Р.В.Лаврик.*

Вперше у розплавах систем $\text{M}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3$ (де M — Na, K) виділено складні фосфати, які містять два різні іони. Підібрано оптимальні умови для вирощування монокристалів сполук $\text{NaMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ та $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$. Проведено рентгено-

структурне дослідження монокристалів синтезованих фосфатів $MMn_6(P_3O_{10})(P_2O_7)_2$ (де М — Na, K). Структура сполук належить до моноклінної сингонії (пр. гр. $P2_1/m$), параметри решітки дорівнюють: $a = 5.350$ (5.358) Å, $b = 26.643$ (26.697) Å, $c = 6.566$ (6.575) Å, $\beta = 107.25^\circ$ (107.22 $^\circ$); $Z = 2$, $\rho = 3.575$ (3.568) г/см 3 відповідно. Синтезовані сполуки досліджено методами: РСА, ДТА, ІЧ- та ЕПР-спектроскопії, магнетохімії, для отриманих фосфатів виміряно залежності діелектричної сталої від температури. Встановлено наявність слабкої антиферромагнітної взаємодії у ланцюжках октаедрів $[MnO_6]$. У результаті проведених досліджень запропоновано ряд фізико-хімічних характеристик синтезованих сполук, які можна використовувати у розробці даних функціональних матеріалів.

1. Introduction

Constant development of science and technology necessitates further studies of new compounds and generation of new materials [1–3]. Recently, scientists have made significant progress in the field of inorganic chemistry of molten salts, in particular, the synthesis of simple and double phosphates of alkali and polyvalent metals [4]. These compounds exhibit a wide range of magnetic, nonlinear optical, catalytic and electrophysical properties, and are used as single crystals and ceramics [5, 6].

Phosphate melts of alkali metals are widely used as media for the synthesis and growing of single crystals of various phosphates and at the same time they are universal solvents of multivalent metal oxides [7]. Directed synthesis of phosphate compounds with various properties dictates in-depth study of their crystalline structure and evaluation of physicochemical properties [5, 8, 9] to be used in the development of new technologies. Investigation of compounds' properties, synthesis and development of materials on their base are of specific interest [10, 11].

The objective of this research is to determine the optimum conditions for the synthesis of double phosphates $MMn_6(P_3O_{10})(P_2O_7)_2$ (where M — Na, K) in the fluxes of $M_2O-P_2O_5-Mn_2O_3$ systems (where M — Na, K) and to investigate their physical and chemical properties.

2. Experimental

The solubility and interactions of manganese oxide (III) in the $Na_2O-P_2O_5-Mn_2O_3$ and $K_2O-P_2O_5-Mn_2O_3$ systems have been studied at temperatures of 800–980°C. Molecular ratios of $M_2O:P_2O_5$ have been changed over the range of 0.5 to 2.0; the content of Mn_2O_3 in original fluxes of the studied system have been changed over the range of 15.0–30.0 wt.%. The mixtures of the $M_2O-P_2O_5-Mn_2O_3$ system have been prepared using anhydrous reagents MPO_3 , $M_4P_2O_7$ and $NH_4H_2PO_4$ (or $(NH_4)_2HPO_4$)

through mixing of their calculated amounts with subsequent dehydration and melting at 800°C. Mn_2O_3 has been introduced into the fluxes at various $M_2O:P_2O_5$ ratios with subsequent melting at elevated temperature in platinum crucibles for 3–4 h with intermittent mixing to the point of constant consistency. Homogenous fluxes have been kept at respective temperatures for 10 h until the establishment of equilibrium between liquid and crystalline phases. Equilibrium liquid phases have been separated from crystalline ones by decantation and the rest of flux has been washed out with hydrochloric acid solution. The content of manganese oxide (III) has been determined in the decanted equilibrium liquid phases.

Optimum conditions for the growing of single crystals of $NaMn_6(P_3O_{10})(P_2O_7)_2$ compound in the flux of $Na_2O-P_2O_5-Mn_2O_3$ system have been observed at the 0.76–0.91 molar ratios of $Na_2O:P_2O_5$. Initial prepared phosphate melts have been saturated with Mn_2O_3 oxide (15.0 wt.%) at 900°C and homogenized for 3 hours. With the gradual lowering of temperature from 920°C to 700°C, single crystals of complex phosphate have been crystallized out of the fluxes within 24 h. Single crystals of $KMn_6(P_3O_{10})(P_2O_7)_2$ have been obtained using similar methods at 0.56–0.66 molar ratios of $K_2O:P_2O_5$, saturated with Mn_2O_3 (30.0 wt.%) over the range of temperatures from 980°C to 700°C. Solid phases have been identified using quantitative chemical and physicochemical analytical methods: XRD, DTA, IR- and EPR-spectroscopy, magnetochemistry; dependence of dielectric constant (ϵ) on the temperature has been assessed.

3. Results and discussion

White crystals of rhombic habit $0.2 \times 0.3 \times 0.1$ mm 3 underwent X-ray diffraction analysis at "Siemens P3/PC" diffractometer excited with Mo irradiation passing through graphite monochromator. The findings of X-ray diffraction study demonstrated that crystalline structure of synthesized phosphates of $MMn_6(P_3O_{10})(P_2O_7)_2$ -type is based

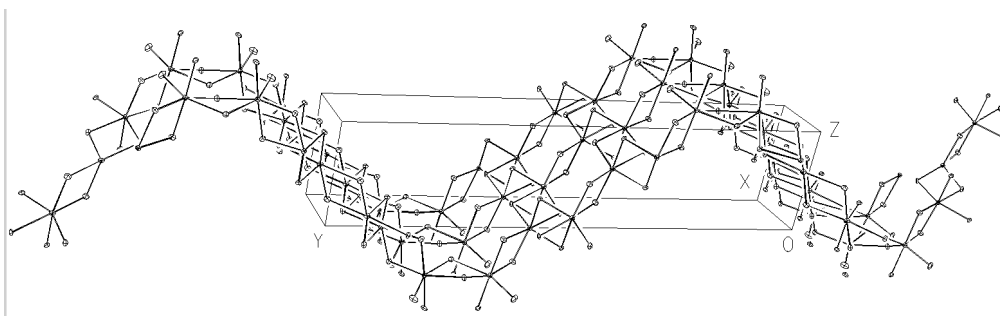


Fig. 1. "Wavy" chains formed of $[\text{MnO}_6]$ in structure $\text{MMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ ($M - \text{Na, K}$).

on the space framework composed of octahedron chains $[\text{MnO}_6]$ joined by edges and tetrahedrons $[\text{PO}_4]$ combined into $[\text{P}_2\text{O}_7]$ and $[\text{P}_3\text{O}_{10}]$ groups. The cavities of the framework contain potassium atoms.

The unit cell of manganese polyhedral chain consists of three distorted octahedra with the length of Mn–O bonds falling within 2.090–2.442 Å. Two "wavy" chains with recurrence interval equal to 12 octahedra $[\text{MnO}_6]$ pass through the unit cell of lattice.

"Wavy" chains formed of $[\text{MnO}_6]$ octahedra have been discovered in the structure of $\text{MMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ (where $M - \text{Na, K}$) [12] (Fig. 1). The presence of such composite structural fragments may affect the physicochemical properties of obtained phosphates.

Interpretation and clarification of the structure have been performed using "SHELX-97" set of programs [13]. $\text{KMn}_6\text{P}_7\text{O}_{24}$ crystals belong to the monoclinic crystal system, (space group $P2_1/m$). The space unit parameters have been further defined using LS method according to 24 reflections within the angular range of $24.0^\circ \leq \theta \leq 40.0^\circ$. Integral intensities have been measured with 2θ method within the angular range of $3.05^\circ \leq \theta \leq 50.07^\circ$ at the scanning rate of 2–29 degrees per min. As a result of experiment, 5515 reflections have been obtained (within $7 \leq h \leq 0$; $-37 \leq k \leq 37$; $-8 \leq l \leq 9$), of which 2587 independent ones with $I > 2\sigma(I)$ have been used in the calculations. Adjustment for Lorentz factor has been applied to the data set, along with empirical absorption correction.

Calculation of the structure of $\text{KMn}_6\text{P}_7\text{O}_{24}$ has been performed with anisotropic approximation of thermal parameters for all the atoms. The terminal value of divergence factor is $R_w = 0.0494$. There are three crystallographically different manganese atoms in the structure of $\text{KMn}_6\text{P}_7\text{O}_{24}$ forming distorted octahedra $[\text{MnO}_6]$. The

relative value of manganese polyhedra deformation has been calculated using the following formula:

$$V = \frac{1}{6} \left(\frac{R_0 - R_c}{R_c} \right).$$

where R_0 — length of Mn–O bond in octahedron; R_c — average length of Mn–O bond in polyhedron MnO_6 . The relative values of deformation for polyhedra Mn(1), Mn(2) and Mn(3) are $2.57 \cdot 10^{-4}$; $1.03 \cdot 10^{-4}$; $4.33 \cdot 10^{-4}$, respectively, and demonstrate the differences between manganese octahedra.

Discrete anions $\text{P}_3\text{O}_{10}^{5-}$ of $\text{KMn}_6\text{P}_7\text{O}_{24}$ structure contain two structurally different atoms of phosphorus — P(3) atom lies within the symmetry plane and P(4) atom — beyond it. Tetrahedron P(3) O_4 is less distorted and characterizes by a slight deviation in the length of P(3)–O(8) and P(3)–O(10) bonds. Tetrahedron P(4) O_4 demonstrates relatively larger distortion since it is characterized by significant variance in the lengths of P(4)–O(10) and P(4)–O(11) bonds, that are about 10 % of the mean P–O bond length. Tetrahedra $[\text{PO}_4]$ combine via bonding atoms O(10) and O'(10) to form the symmetric anion $\text{P}_3\text{O}_{10}^{5-}$ characterized by the angle P(3)–O(10)–P(4) of 137.70° . Two phosphate tetrahedra P(1) O_4 and P(2) O_4 combine via oxygen atom O(4) to form the $[\text{P}_2\text{O}_7]$ group characterized by slightly longer, nearly similar lengths of P–O bonds to the bonding atom, and insignificant differences in the lengths of bonds to the opposite oxygen atoms P(1)–O(1) and P(2)–(7) — 1.490 and 1.525(6) Å, respectively. The anionic group $[\text{P}_2\text{O}_7]$ consists of nearly regular tetrahedra $[\text{PO}_4]$ and is characterized by the P(1)–O(4)–P(2) angle of 150.52° .

The nearest-neighbor environment of Na and K atoms in the $\text{MMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ structure consists of six end atoms of oxygen of two groups $[\text{P}_3\text{O}_{10}]$ with symmetric placement relative to the symmetry plane.

Table. IR-spectroscopy of phosphates (cm⁻¹)

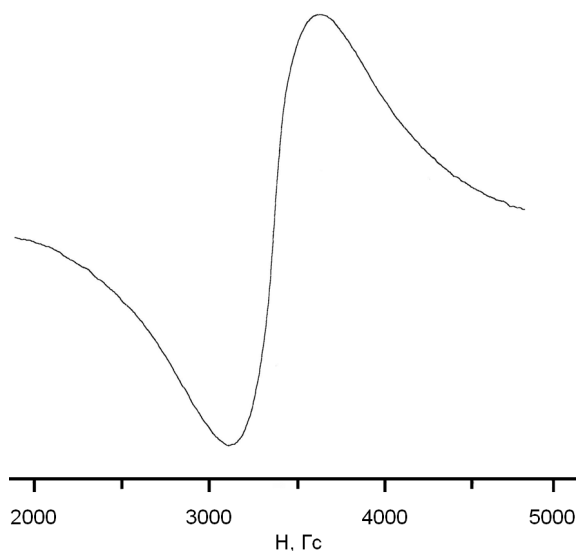
Igning frequencies	Formula	
	NaMn ₆ P ₇ O ₂₄	KMn ₆ P ₇ O ₂₄
τ (PO ₃)	420 sh.	420 w.
fluct. lattice	435 sh.	430 sh.
	490 w.	490 sh.
δ _s	520 sh.	520 sh.
P–O	5405 w.	535 w.
δ _{as}	555 sh.	555 sh.
+ ν MO	570 w.	570 w.
	605 w.	605 w.
ν _s P–O–P	700 str.	700 str.
	715 w.	715 w.
ν _s PO ₄	950 str.	950 str.
ν _{as} PO ₄	985 str.	985 str.
	995 w.	995 w.
ν _s PO ₂	1060 w.	1060 w.
	1100 w.	1100 w.
	1110 sh.	1110 sh.

However, there are another four oxygen atoms located at longer distances (about 3.2 Å), which can also be counted as coordination polyhedron of alkali-metal atoms. Thus, the coordination number of alkali metal in the MMn₆(P₃O₁₀)(P₂O₇)₂ structure is 10.

Isostructurality of complex double phosphates NaMn₆(P₃O₁₀)(P₂O₇)₂ and KMn₆(P₃O₁₀)(P₂O₇)₂ is also supported by the findings of IR-spectroscopy (Table). Infrared spectra of have been studied using spectrophotometers UR-20 and UR-10 (Carl Zeiss) in the KBr tablets.

In order to confirm the presence of Mn²⁺ in the double phosphates with various phosphate anions we have studied the EPR spectra using polycrystalline samples. Fig. 2 shows the EPR spectra of polycrystals of NaMn₆(P₃O₁₀)(P₂O₇)₂ double phosphate obtained at 23°C using "PS 100-X" spectrometer. The spectral lines have specific widening due to a weak exchange between paramagnetic centers [MnO₆] in octahedral chain. The calculated values of tensor *g* for the synthesized phosphates agree with the results of magnetochemical studies and fall within 1.98–1.99. The obtained spectra of electronic paramagnetic resonance for the synthesized double phosphates of manganese (II) are typical and specific [5, 14].

Thermal tests have been performed with derivatograph Q-1500 (Hungary). The sam-

Fig. 2. EPR spectrum of NaMn₆(P₃O₁₀)(P₂O₇)₂.

ple was heated at a temperature range of 20–1000°C under dynamic temperature elevation mode using cylindrical platinum crucibles (sample weight: 0.300 g; heating rate: 5 deg/min. According to derivatographic analysis, NaMn₆(P₃O₁₀)(P₂O₇)₂ and KMn₆(P₃O₁₀)(P₂O₇)₂ compounds are rather stable and do not melt at the temperatures up to 1000°C. When heated under dynamic conditions with the rate 5 deg./min, the compounds don't lose their mass, which is also indicative of Manganese (II) content in the double phosphates.

The identified magnetochemical properties of the compounds result from the X-ray characteristics of synthesized phosphates due to their distinct structural features — the presence of octahedral chains of manganese. Magnetochemical properties of the resulting compounds have been studied using Faraday method over the range of 3–400 K (Manics DSM-8 magnetometer, Switzerland); the diamagnetic correction calculated with Pascal constant has been taken into account in the evaluation of magnetic susceptibility of the compounds. Temperature dependence of the magnetic susceptibility product χT and temperature for KMn₆(P₃O₁₀)(P₂O₇)₂ and NaMn₆(P₃O₁₀)(P₂O₇)₂ compounds is given in Fig. 3. The χT value for KMn₆(P₃O₁₀)(P₂O₇)₂ obtained at room temperature is 11.8 Bohr magneton (μ_B) that is lower than the theoretical value (17.74 Bohr magneton). The χT value changes slowly, if at all, within the temperature range 300–100 K, and sharp decrease in the magnetic susceptibility within

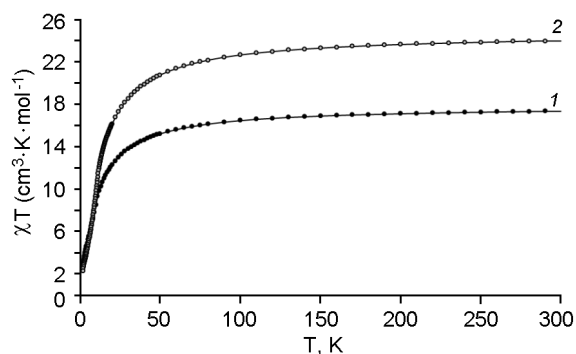


Fig. 3. Temperature dependences of the magnetic susceptibility product χT and temperature for compounds: 1 — $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$; 2 — $\text{NaMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$.

100–4 K is indicative of the antiferromagnetic interaction between the magnetic centers of manganese.

The quantitative analysis of magnetic susceptibility data of synthesized phosphates has been performed in view of assumed isotropic interaction between magnetic centers using spin-system Hamiltonian:

$$H = J(S_{\text{Mn}1} \cdot S_{\text{Mn}2} + S_{\text{Mn}2} \cdot S_{\text{Mn}3} + S_{\text{Mn}3} \cdot S_{\text{Mn}1}).$$

The best agreement of the experimental results with theoretical data within the temperature range 4–40 K was obtained at $J = 0.70(7) \text{ cm}^{-1}$ and $g = 1.99$ values and consistency index $R^2 = 0.995$. The χT value of the double phosphate $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ changes slowly, if at all, within the temperature range 100–300 K. The decrease in χT value is more significant at the temperatures below 100 K, which is indicative of the weak antiferromagnetic interaction between the triangles of manganese (Fig. 4).

The synthesized compounds have been studied for the dielectric constant (ϵ) — temperature relation. The increase in (ϵ) with elevated temperatures is rather typical for the dielectrics, i.e. ion conductors (polycor sample — curve (1), Fig. 5).

Complex double phosphates $\text{NaMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ and $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ demonstrate abnormal thermal dependence of (ϵ) within the range of 60–100°C — decrease in dielectric constant (curves (2) and (3), Fig. 5). This may be attributable to the weak interaction between paramagnetic centers in the structure of $\text{MMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ -type phosphates. With the elevation of temperature, the values of dielectric constant increase, which indicates that obtained compounds of $\text{MMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ -type can be used as functional materials.

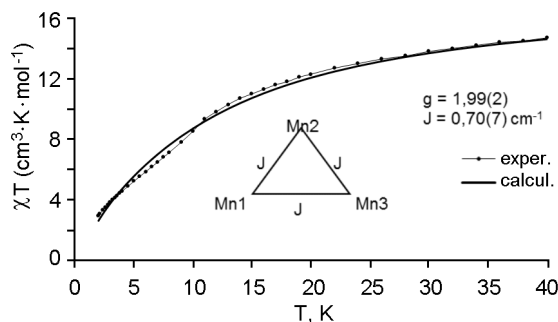


Fig. 4. Magnetic susceptibility product χT — temperature relation for compound $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$.

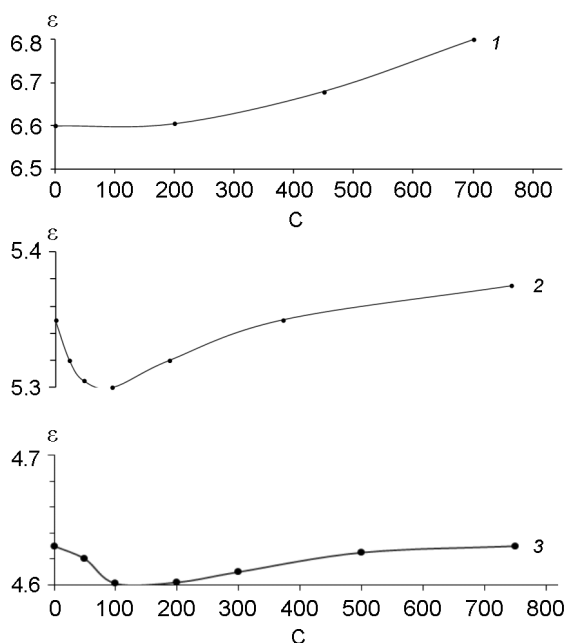


Fig. 5. Dielectric constants (ϵ) — temperature relation: 1 — polycor, 2 — $\text{NaMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$, 3 — $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$.

4. Conclusions

Complex phosphates $\text{MMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ containing two different ions have been identified in the fluxes of $\text{M}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3$ systems (where M — Na, K) over a temperature range of 800–980°C. During experiments, optimum conditions for the growing of single crystals of compounds from fluxes have been selected; their physicochemical properties have been studied. XRD, IR- and EPR-spectroscopy analytical methods proved the isostructurality and similarity of the synthesized phosphates $\text{NaMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ and $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$. Complex XRD has been performed, which allowed for the identification of several structural features of

the synthesized $\text{MMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ phosphates, namely the presence of "wavy" chains with recurrence interval equal to 12 octahedra $[\text{MnO}_6]$. Established spectrum of physicochemical properties of synthesized phosphates $\text{NaMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ and $\text{KMn}_6(\text{P}_3\text{O}_{10})(\text{P}_2\text{O}_7)_2$ demonstrates the possibility of their use in the development of functional materials, which can be utilized in various fields of science and technology.

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