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V.I. Maksin^a, *R.V. Lavrik*^a, *T.I. Ushchapivska*^a, *O.V. Petrenko*^b**GROWING OF SINGLE-CRYSTALS OF DOUBLE SODIUM-MANGANESE(II) PYROPHOSPHATE**^a National University of Life and Environmental Sciences of Ukraine, Kyiv, Ukraine^b Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

Single crystals of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ compound have been first obtained during the examination of interaction in the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3-\text{NaF}$ (10 wt.%) system in the fluxes with $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ molar ratios ranging from 0.52 to 0.76 (saturated with manganese(III) oxide 25.0–32.0 wt.%) at the temperatures of 960–880°C. Optimum conditions for the synthesis and growing of single crystals of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ compound have been determined. Complete X-ray diffraction analysis of the synthesized phosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ has been performed. According to its structure, the double phosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ belongs to the triclinic crystal system, spatial grid $\text{P}\bar{1}$; lattice parameters are as follows: $a=5.359 \text{ \AA}$, $b=6.563 \text{ \AA}$, $c=16.299 \text{ \AA}$, $\alpha=81.29^\circ$, $\beta=82.70^\circ$, $\gamma=72.44^\circ$, $V=538.23 \text{ \AA}^3$, $Z=4$, $c_{\text{calc}}=3.447 \text{ g cm}^{-3}$. Structural features of synthesized phosphate have been determined. The structure is composed of continuous chain of distorted octahedra $[\text{MnO}_6]$ spacing along the direction *ob*. Diphosphate groups of tetrahedra $[\text{PO}_4]$ divide the chains $[\text{MnO}_6]$ and also run along *ob* direction. Pairwise linked pentagonal bipyramids of sodium divide the «units» of polyhedral of manganese and phosphorus, filling the channels along *oy* axis. The crystalline structure of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ includes three nonequivalent, according to their crystallography, octahedra of manganese with slightly distorted form. The compound has been studied using X-ray diffraction and X-ray phase analyses, differential thermal analysis, IR spectroscopy and complete chemical analysis.

Keywords: double phosphate, IR-spectroscopy, X-ray diffraction analysis, X-ray phase analysis, growing of single crystals, crystallization, flux.

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Introduction

Contemporary developments in science and technology require research and the use of new materials based on phosphate compounds [1,2]. Double phosphates of alkali and 3d transition metals may exhibit a range of valuable physical and chemical properties. Phosphate compounds may possess catalytic, magnetic, electrophysical, non-linear optical properties; they are widely used as monocrystals or polycrystals, ceramics, etc. [3–5].

The tailor-made synthesis of double phosphates of alkali and multivalent metals is the basis for the in-depth research of physical and chemical properties, composition and structure of the compounds to be used for the development of new materials [6,7]. Many phosphate compounds with the structure of a well-known nonlinear optical crystal KTP and double polyphosphates are successfully used

right now. Investigation of the properties of compounds as well as their synthesis and development of materials on their base are the areas of special scientific interest [6–9].

One of the most commonly used techniques of obtaining double phosphates of alkali and 3d-metals is the synthesis of compounds from the fluxes of phosphate and fluoride phosphate systems of alkali metals by spontaneous crystallization with slow cooling [6,9–11]. Systems of $\text{M}_2\text{O}-\text{P}_2\text{O}_5-\text{Me}_x\text{O}_y$ -type (where $\text{M}=\text{Li}, \text{Na}, \text{K}$) are known to be not only universal solvents of 3d-metal oxides, but also reaction media for the synthesis of various double phosphates [10,11]. This technique has some advantages over the other methods and makes it possible to obtain, by using programmable cooling, substances in the form of high-quality and high-purity crystals with high yield of interaction products,

which in turn has impact on physical and chemical properties of the synthesized substances.

The purpose of this study is to determine optimum conditions for the synthesis of double polyphosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ and investigate its physical and chemical properties.

Experimental

Reagents, synthesis and methods

Single crystals of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ compound was obtained during the examination of interaction in the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3-\text{NaF}$ (10 wt.%) system in the fluxes with $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ molar ratios ranging from 0.52 to 0.76 (saturated with manganese (III) oxide 25.0–32.0 wt.%) at 960–880°C.

The initial mixtures of $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3$ system (with baseline $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ molar ratios of 0.5–1.5) have been prepared by mixing the calculated quantities of anhydrous reagents NaPO_3 , $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{NH}_4\text{H}_2\text{PO}_4$ (or $(\text{NH}_4)_2\text{HPO}_4$), with subsequent dehydration and melting at 800–850°C. Mn_2O_3 was added to the fluxes with various $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ ratios followed by their melting at elevated temperatures in platinum crucibles for 2–4 hours with intermittent mixing until homogeneity was obtained, with subsequent addition of the calculated quantity of NaF and homogenizing the fluxes. The homogenous fluxes have been kept at appropriate temperatures for 7–8 hours until the establishment of equilibrium between the liquid and crystal phases.

Phase equilibriums in the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3$ system have been studied using visual-polythermal method. Equilibrium liquid phases have been separated from crystal ones by decantation with washing out of residue flux using diluted solutions of mineral acids. Solid phases have been identified using quantitative chemical and physicochemical methods of analysis. The content of manganese(III) oxide has been determined in the decanted equilibrium liquid phases.

The contents of manganese(III) oxide in the equilibrium liquid phases of the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3$ system with various molar ratios of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ at 900°C and 950°C are shown in Fig. 1. The solubility curves of manganese(III) oxide demonstrate two distinct extrema, indicative of complex chemical interaction within the system. The maximum solubility of Mn_2O_3 in $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3$ system is 30.80 wt.% for the flux with the $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ molar ratio of 0.55.

Optimum conditions for single crystals growing of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ with the size of 0.5–2 mm have been determined. The fluxes with the weight of 7 g and $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ molar ratio of 0.52 have been saturated with manganese (III) oxide (3.0 g) at 950°C

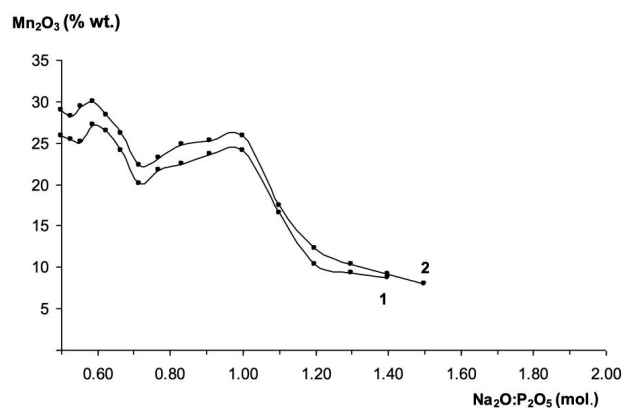


Fig. 1. Mn_2O_3 solubility isotherms in the fluxes of the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3-\text{NaF}$ system: 1 – 900°C (10 wt.% NaF); 2 – 950°C (20 wt.% NaF)

and homogenized for 3 hours with subsequent addition of NaF (20 wt.%) and homogenizing for 1 hour. With gradual lowering of temperature from 960°C to 880°C, the single crystals of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ have been obtained from the fluxes within 24 hours, washed free from flux residues using the diluted hydrochloric acid solution and washed out with water and dried at room temperature. Light-brown crystals up to 2 mm in size have been obtained.

The structure of novel double phosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ has been performed using X-ray diffraction method. X-ray diffraction analysis of light-brown lamellar crystals 0.2×0.5×0.3 mm in size has been performed using 4-circle Enraf-Nonius CAD 4 diffractometer (MoK_α -radiation, graphite monochromator). According to their structure, crystals belong to triclinic crystal system, space group $\text{P}\bar{1}$. The lattice parameters are as follows: $a=5.359(3)$ Å, $b=6.563(0)$ Å, $c=16.299(3)$ Å, $\alpha=81.28^\circ$, $\beta=82.69^\circ$, $\gamma=72.43^\circ$, $V=538.23$ Å³, $Z=4$, $c_{\text{calc}}=3.447$ g/cm³ [11].

The integrated intensity has been measured using $2\theta:\theta$ method over the range of angles $2.54^\circ \leq 2\theta \leq 55.05^\circ$ at the scan rate of 2–18 degrees per minute. As a result of experiment, 2019 reflections (within $-6 \leq h \leq 0$, $-7 \leq k \leq 7$, $-19 \leq l \leq 19$) have been obtained, of which 1819 independent reflections with $I > 2\sigma(I)$ have been used for calculations.

Results and discussion

When comparing the content of Mn_2O_3 in the equilibrium liquid phases of the studied $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3-\text{NaF}$ (10 wt.%) system at 900°C and 950°C, a decrease in the solubility of manganese (III) oxide can be observed with larger molar ratios of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ (1.0–1.5).

Lorenz factor correction and empirical absorption correction have been applied to the dataset when processing the results of X-ray diffraction

Table 1

Coordinates of atoms and equivalent thermal corrections for the $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ structure

Atom	Coordinates of atoms x/a ($\times 10^4$)	Coordinates of atoms y/b	Coordinates of atoms z/c ($\times 10^4$)	Equivalent thermal corrections (U_{eq}), ($\text{\AA}^2 \cdot 10^3$)
Mn(1)	5306(1)	6283(1)	3077(1)	10(1)
Mn(2)	2534(1)	10320(1)	1639(1)	10(1)
Mn(3)	6718(1)	12904(1)	775(1)	13(1)
Na(1)	5850(3)	2514(3)	4821(1)	25(1)
Na(2)	1115(3)	12832(3)	3626(1)	23(1)
P(1)	11335(2)	5632(1)	1783(1)	8(1)
P(2)	7854(2)	7836(1)	391(1)	7(1)
P(3)	9316(2)	7500(1)	4209(1)	9(1)
P(4)	6848(2)	10925(1)	2858(1)	8(1)
O(1)	13194(5)	3462(4)	1592(2)	10(1)
O(2)	12864(5)	7016(4)	2043(2)	12(1)
O(3)	9070(5)	5410(4)	2383(2)	17(1)
O(4)	10375(5)	6813(4)	907(2)	16(1)
O(5)	6411(5)	6178(4)	375(2)	14(1)
O(6)	9180(5)	8428(4)	457(2)	11(1)
O(7)	6146(5)	9772(4)	803(2)	10(1)
O(8)	8240(5)	8583(4)	4987(2)	18(1)
O(9)	12243(5)	6408(4)	4145(2)	15(1)
O(10)	7725(5)	6053(4)	4063(2)	15(1)
O(11)	9061(5)	9403(4)	3432(2)	14(1)
O(12)	5623(5)	12879(4)	3322(2)	14(1)
O(13)	8401(5)	11358(4)	2041(2)	10(1)
O(14)	4809(5)	9760(4)	2796(2)	12(1)

analysis. Lattice parameters have been refined using full-matrix least-squares method according to 20 reflections over the range of angles $14^\circ \leq \theta \leq 24^\circ$. The structure has been calculated with anisotropic approximation of thermal parameters for all of the atoms. The final value of the divergence factor is $R_w = 0.0693$. The positional parameters of atoms with standard deviations are given in Table 1.

Figure 2 demonstrates the general projection of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ structure on yz plane. The structure

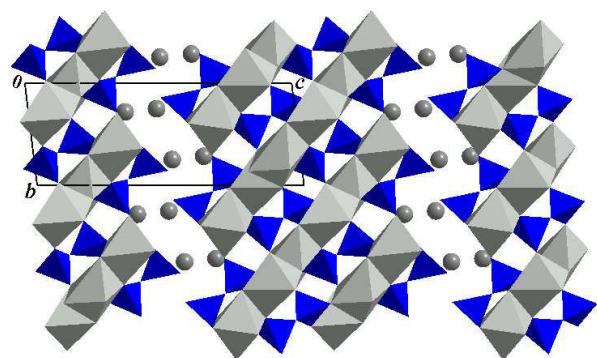


Fig. 2. Projection of the $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ structure on yz plane

is composed of continuous chain of distorted octahedra $[\text{MnO}_6]$ spacing along the direction. Diphosphate groups of tetrahedra $[\text{PO}_4]$ divide the chains $[\text{MnO}_6]$ and also run along ob direction. Pairwise linked pentagonal bipyramids of sodium divide the «units» of polyhedral of manganese and phosphorus, filling the channels along oy axis.

According to its structure, $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ belongs to the triclinic crystal system, spatial grid $P\bar{1}$; the lattice parameters are as follows: $a = 5.359 \text{ \AA}$, $b = 6.563 \text{ \AA}$, $c = 16.299 \text{ \AA}$, $\alpha = 81.29^\circ$, $\beta = 82.70^\circ$, $\gamma = 72.44^\circ$, $V = 538.23 \text{ \AA}^3$, $Z = 4$, $c_{\text{calc}} = 3.447 \text{ g/cm}^3$. The crystalline structure of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ includes three nonequivalent, according to their crystallography, octahedra of manganese with slightly distorted form (Table 1). The length of links between manganese and oxygen atoms in polyhedra $[\text{MnO}_6]$ varies within the following ranges: $\text{Mn}(1)\text{--O}$ (2.144–2.229 \AA), $\text{Mn}(2)\text{--O}$ (2.129–2.229 \AA) and $\text{Mn}(3)\text{--O}$ (2.111–2.321 \AA) (Table 2).

$\text{Mn}(1)$ and $\text{Mn}(2)$ octahedra share the edges $\text{O}(2)\text{--O}(14)$, and $\text{Mn}(2)$ and $\text{Mn}(3)$ have common edges $\text{O}(6)\text{--O}(13)$. $\text{Mn}(2)\text{O}_6$ polyhedron demonstrates significant shift towards $\text{Mn}(3)\text{O}_6$, which impacts the distances between the atoms of

Table 2

Lengths of bonds in the $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ structure

Bond	Lengths of bonds, Å	Bond	Lengths of bonds, Å
Mn(1)–O(3)	2.144(3)	Mn(2)–O(1)#6	2.184(2)
Mn(1)–O(2)#2	2.172(2)	Mn(3)–O(5)#7	2.111(3)
Mn(1)–Na(2)#3	3.386(0)	Mn(3)–O(7)	2.161(2)
Mn(1)–Na(2)#1	3.594(9)	Na(1)–O(12)#1	2.434(3)
Mn(2)–O(6)#5	2.178(3)	Na(1)–O(10)#4	2.531(3)
Mn(2)–O(14)	2.299(2)	Na(1)–P(3)#4	3.009(8)
Mn(3)–O(1)#6	2.137(2)	Na(1)–Na(2)#3	3.261(2)
Na(1)–O(9)#9	2.370(3)	Na(2)–O(12)	2.412(3)
Na(1)–O(8)#1	2.500(3)	Na(2)–O(14)	2.748(3)
Na(1)–O(9)#2	2.862(3)	Na(2)–P(4)	3.122(5)
Na(1)–Na(1)#4	3.235(3)	Na(2)–P(1)#6	3.283(9)
Na(2)–O(8)#10	2.336(3)	P(1)–O(1)	1.523(2)
Na(2)–O(3)#6	2.565(3)	P(1)–Na(2)#3	3.283(9)
Na(2)–O(9)#6	2.859(3)	P(2)–O(6)	1.524(3)
Na(2)–Na(1)#6	3.261(2)	P(3)–O(9)	1.513(3)
P(1)–O(3)	1.487(3)	P(3)–Na(1)#4	3.009(8)
P(1)–O(4)	1.586(3)	P(4)–O(13)	1.514(2)
P(2)–O(5)	1.518(3)	P(4)–O(11)	1.601(3)
P(3)–O(8)	1.511(3)	O(1)–Mn(3)#3	2.137(2)
P(3)–O(11)	1.626(3)	O(2)–Mn(1)#11	2.172(2)
P(3)–Na(1)#9	3.198(3)	O(6)–Mn(3)#8	2.134(2)
P(4)–O(14)	1.531(2)	O(8)–Na(1)#4	2.476(3)
P(4)–Na(1)#7	3.443(2)	O(9)–Na(1)#9	2.370(3)
O(2)–Mn(2)#11	2.129(2)	O(10)–Na(2)#3	2.467(3)
O(5)–Mn(3)#1	2.111(3)	O(12)–Mn(1)#7	2.168(2)
O(8)–Na(2)#10	2.336(3)	Mn(1)–O(12)#1	2.168(3)
O(9)–Mn(1)#11	2.229(3)	Mn(1)–O(9)#2	2.229(3)
O(9)–Na(1)#11	2.862(3)	Mn(1)–Na(1)#4	3.567(3)
O(11)–Na(2)#11	2.859(3)	Mn(2)–O(13)#2	2.158(2)
O(13)–Mn(2)#11	2.158(2)	Mn(2)–O(7)	2.189(2)
Mn(1)–O(10)	2.151(3)	Mn(3)–O(6)#8	2.134(2)
Mn(1)–O(14)	2.199(2)	Mn(3)–O(13)	2.321(2)
Mn(1)–Na(1)	3.454(8)	Na(1)–O(8)#4	2.476(3)
Mn(2)–O(2)#2	2.129(2)	Na(1)–O(10)	2.856(3)

3d-metal: Mn(1)–Mn(2) \sim 3.40 Å and Mn(2)–Mn(3) \sim 3.26 Å. Due to this shift, the chain consisting of three octahedra bends, and its repetitions in the structure lead to the formation of continuous chains along *ob* direction (Fig. 2). Various degrees of deformity of manganese polyhedron are accentuated by the circles, formed by axially oriented atoms of oxygen and central atom of octahedron: $\angle\text{O}(2)\text{--Mn}(1)\text{--O}(9)$ 159.53° , $\angle\text{O}(6)\text{--Mn}(2)\text{--O}(14)$ 164.64° and $\angle\text{O}(5)\text{--Mn}(3)\text{--O}(13)$ 119.10° .

The structure of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ includes two differing by their crystallography diphosphate groups $[\text{P}_2\text{O}_7]$ consisting of phospho oxygen tetrahedra $[\text{PO}_4]$, sharing common apical atoms O(4) and O(11). The angles at bridging oxygen atoms in $[\text{P}_2\text{O}_7]$ groups

lie in opposite directions and make: P(1)–O(4)–P(2) 144.07° and P(3)–O(11)–P(4) 138.33° (Fig. 3). The average length of P–O link in the first bridge is 1.592 Å, and it is 1.613 Å in the second one. It is evident that the increase in the length of P–O links in P(3)–O(11)–P(4) section is due to the participation of O(8) and O(12) atoms in the coordination to Na(1) and Na(2) atoms, respectively.

The channels filled with sodium polyhedra run along *oy* axis between the structure blocks made of $[\text{MnO}_6]$ and $[\text{PO}_4]$ polyhedra. Sodium cations are located near the $z=1/2$ plane and make curved pentagonal bipyramids with oxygen atoms at the vertices. Pairwise linked bipyramids $[\text{NaO}_7]$ fill the channels in the $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ structure along *ob*

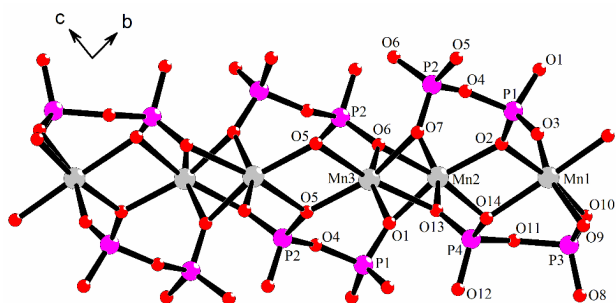


Fig. 3. Coordination environment of manganese atoms in the $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ structure

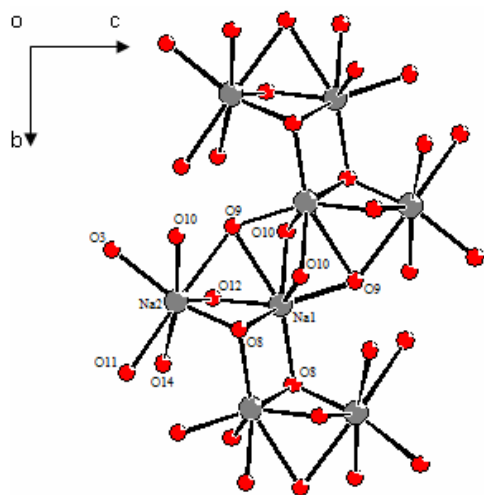


Fig. 4. Surroundings of sodium atoms in the $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ structure

direction (Fig. 4).

It is notable that only one atom of oxygen of $\text{Mn}(1)\text{O}_6$ octahedron takes part in the coordination to atoms of alkali metal. Polyhedron $\text{Na}(1)\text{O}_7$ is very distorted: the angle between axially oriented atoms of oxygen $\angle\text{O}(9)\text{--Na}(1)\text{--O}(8)$ is 156.96° . At the same time, the lengths of links between $\text{Na}(1)\text{--O}(9)$ and $\text{Na}(1)\text{--O}(8)$ atoms slightly differ and are equal to 2.862 \AA and 2.470 \AA , respectively. Equatorial atoms of oxygen form a distorted pentagon. The lengths of $\text{Na}(1)\text{--O}$ links in pentagonal bipyramid $[\text{NaO}_7]$ range within $2.370\text{--}2.862 \text{ \AA}$. Polyhedron $\text{Na}(2)\text{O}_7$ is less distorted: the length of links in the fragment $\text{O}(11)\text{--Na}(2)\text{--O}(9)$ (angle makes 166.43°) is similar and

equals to 2.859 \AA . Pentagonal bipyramids $\text{Na}(1)\text{O}_7$ and $\text{Na}(2)\text{O}_7$ share a common face (Fig. 4) formed by $\text{O}(9)\text{--O}(12)\text{--O}(8)$ atoms. This link imparts additional strength to the structure of double phosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$.

A complete chemical analysis proved the chemical composition of the synthesized compound $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ (Table 3).

Infrared spectra of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ were recorded using UR-20 and UR-10 spectrophotometer (Carl Zeiss) and KBr pellets. The characteristic vibrations $\tau(\text{PO}_3)$ $420; 500 \text{ cm}^{-1}$; $\delta_s, \delta_{as}(\text{P--O}) + \nu(\text{MO})$ $540; 560; 590 \text{ cm}^{-1}$; $\nu_s(\text{P--O--P})$ $720; 800 \text{ cm}^{-1}$ and $\nu_{as}(\text{P--O--P})$ 920 cm^{-1} correspond to and are typical of polyphosphates [7,9]. Characteristic vibrations $\nu_s(\text{P--O--P})$ at $700\text{--}800 \text{ cm}^{-1}$ are indicative of the presence of polyphosphate chains made of $[\text{PO}_4]$ tetrahedra in the structure of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ double phosphate.

Thermal analysis of the synthesized phosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ have been performed using Q-1500 Paulik derivatograph (Hungary). The sample was heated within the range of $20\text{--}1000^\circ\text{C}$ with dynamic elevation of temperature in platinum cylindrical crucibles (the weighed portion was 0.310 g and the heating rate was 5 degrees per minute). The derivatographic analyses showed that double phosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ is subject to congruent melting at 785°C .

Conclusions

The crystallization region of new double phosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ has been determined in the fluxes of the $\text{Na}_2\text{O--P}_2\text{O}_5\text{--Mn}_2\text{O}_3\text{--NaF}$ system (10 and $20 \text{ wt.}\%$) at $800\text{--}950^\circ\text{C}$. In addition, optimum conditions for the high-yield (more than 45%) growing of single crystals of compound have been selected. The series of their physical and chemical properties have been studied and the melting temperature of compound (785°C) has been determined. A complete X-ray diffraction analysis of the synthesized phosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ has been performed along with the identification of its structural features. «Bending-over» of the chain of three octahedra, which repetition in the structure leads to the formation of continuous chains along the oy axis, and the presence of sodium polyhedra $[\text{NaO}_7]$ in the structure with unusual coordination

Table 3

Results of chemical analysis of the synthesized compound

Content of Na_2O , wt.%		Content of MnO , wt.%		Content of P_2O_5 , wt.%	
calculated	found	calculated	found	calculated	found
11.09	11.34	38.10	38.21	50.81	50.45

number 7. The findings of this study can encourage further investigation of the compound as well as development of materials on its base.

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ВИРОЩУВАННЯ МОНОКРИСТАЛІВ ПОДВІЙНОГО НАТРІЙ-МАНГАН(II) ДИПІРОФОСФАТУ

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При дослідженні взаємодії в системі $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3-\text{NaF}$ (10 мас.%) в розплавах у діапазоні мольних співвідношень $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ 0,52–0,76 (насичених манган(III) оксидом 25,0–32,0 мас.%) в інтервалі температур 960–880°C було вперше одержано монокристали сполуки $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$. Підібрані оптимальні умови для синтезу та вирощування монокристалів сполуки $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$. Здійснено повне рентгеноструктурне дослідження синтезованого фосфату $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$. Структура подвійного фосфату $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ належить до триклинної сингонії, пр. гр. $\text{P}\bar{1}$; параметри кристалічної решітки дорівнюють: $a=5,359 \text{ \AA}$, $b=6,563 \text{ \AA}$, $c=16,299 \text{ \AA}$, $\alpha=81,29^\circ$, $\beta=82,70^\circ$, $\gamma=72,44^\circ$, $V=538,23 \text{ \AA}^3$, $Z=4$, $c_{\text{розп}}=3,447 \text{ г/см}^3$. Встановлені особливості будови синтезованого фосфату. Структура складається з нескінченних ланцюжків з деформованих октаедрів $[\text{MnO}_6]$, які проходять уздовж напрямку *ob*. Дифосфатні групи з тетраедрів $[\text{PO}_4]$ розділяють ланцюжки $[\text{MnO}_6]$ і теж орієнтовані вздовж напрямку *ob*. Попарно з'єднані пентагональні біпіраміди натрію розділяють «блоки» з поліедрів мангану та фосфору, заповнюючи канали вздовж осі *oy*. Кристалічна структура містить три кристалографічно нееквівалентні октаедри мангану, які мають дещо деформовану форму. Сполука досліджена методами рентгеноструктурного і рентгенофазового аналізів, диференціального термічного аналізу, ІЧ-спектроскопії, виконано її повний хімічний аналіз.

Ключові слова: подвійний фосфат, ІЧ-спектроскопія, рентгеноструктурний аналіз, рентгенофазовий аналіз, вирощування монокристалів, кристалізація, розплав.

GROWING OF SINGLE-CRYSTALS OF DOUBLE SODIUM-MANGANESE(II) PYROPHOSPHATE

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Single crystals of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ compound have been first obtained during the examination of interaction in the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Mn}_2\text{O}_3-\text{NaF}$ (10 wt.%) system in the fluxes with $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ molar ratios ranging from 0.52 to 0.76 (saturated with manganese(III) oxide 25.0–32.0 wt.%) at the temperatures of 960–880°C. Optimum conditions for the synthesis and growing of single crystals of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ compound have been determined. Complete X-ray diffraction analysis of the synthesized phosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ has been performed. According to its structure, the double phosphate $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ belongs to the triclinic crystal system, spatial grid $\text{P}\bar{1}$; lattice parameters are as follows: $a=5.359 \text{ \AA}$, $b=6.563 \text{ \AA}$, $c=16.299 \text{ \AA}$, $\alpha=81.29^\circ$, $\beta=82.70^\circ$, $\gamma=72.44^\circ$, $V=538.23 \text{ \AA}^3$, $Z=4$, $c_{\text{calc}}=3.447 \text{ g cm}^{-3}$. Structural features of synthesized phosphate have been determined. The structure is composed of continuous chain of distorted octahedra $[\text{MnO}_6]$ spacing along the direction *ob*. Diphosphate groups of tetrahedra $[\text{PO}_4]$ divide the chains $[\text{MnO}_6]$ and also run along *ob* direction. Pairwise linked pentagonal bipyramids of sodium divide the «units» of polyhedral of manganese and phosphorus, filling the channels along *oy* axis. The crystalline structure of $\text{Na}_2\text{Mn}_3(\text{P}_2\text{O}_7)_2$ includes three nonequivalent, according to their crystallography, octahedra of manganese with slightly distorted form. The compound has

been studied using X-ray diffraction and X-ray phase analyses, differential thermal analysis, IR spectroscopy and complete chemical analysis.

Keywords: double phosphate; IR-spectroscopy; X-ray diffraction analysis; X-ray phase analysis; growing of single crystals; crystallization; flux.

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