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SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF OLIGOMERIC, POLYMERIC AND CYCLIC CONDENSED PHOSPHATES

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ABSTRACT: Inorganic polymers – condensed phosphates of polyvalent metals, especially double phosphates containing alkali metals possesses a number of rather interesting and precious properties, which explains projections of their application. The presented work is the result of synthesis, analysis, examination of the experimental data, investigation, determination and evaluation of properties of obtained compounds, especially of double condensed phosphates of trivalent and monovalent metals. We have synthesized about 80 new formerly unknown new condensed phosphates from solution-melts of polyphosphoric acids during investigation of multi-component systems at the temperature range 100-600°C. The examination of some obtained condensed phosphates of alkaline and polyvalent metals for use as ion-exchange materials is important and attractive.

KEYWORDS: Synthesis; Inorganic polymers; Condensed Phosphate; Cyclophosphate, Polyphosphate.

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1. INTRODUCTION

Condensed compounds – in fact so called new inorganic polymers - are predestined to play an even greater role in our "high-tech" society in the future than they have in the past. This conclusion is based upon the trend of increasing applications resulting from the electronic structures of these materials that lead to their unusual optical, magnetic, electrical and chemical properties so adaptable to the demands now being placed on materials [1-4]. Starting from the avant-gardist studies of researchers a lot of number of condensed compounds – inorganic polymers was synthesised in the world. A significant original researches in XX Century are really valuable and was appreciated [6-10]. Among the many processes of condensation of phosphoric anions, one of them leads to the prior arrangement of cyclic, oligomeric or polymeric structures. Inorganic polymers – condensed phosphates of polyvalent metals, especially double phosphates containing alkali metals possesses a number of rather interesting and treasured properties, which explains prospects of their application. A great number very interesting and innovative researches in the field of phosphate's chemistry, mainly in the domain of chemistry of condensed phosphates of Rare Earths and other tri- and polyvalent metals has begun in the nineteenth and twentieth centuries[1-2]. The German school of chemistry has been very dynamic and influential in the domain of phosphates. As we have repeatedly noted in our early publications, starting from the pioneer works of Berzelius, Clark and Graham the German chemists elaborated a lot of number of condensed phosphates; a great number of inventor investigations of this epoch are really appreciated and esteemed [1-4]. In the XX century more serious attention of researchers was dedicated as well to the chemistry of condensed compounds of phosphorus. Consequently, later on, during the past century the field of phosphates' chemistry, particularly the chemistry of condensed phosphates developed much promptly, caused by the development of totally new techniques of analysis, innovator approach to the subject, also of the significance and great importance of applications of phosphates materials in various domain [5-10]. The very important properties: the high thermal stability, significant content of phosphorus - these preconditions have caused their application as raw components for manufacture of phosphate glasses; the use of crystalline and non-crystalline ultraphosphates in quantum electronics are predetermined by their specific properties. Among a varieties of condensation schemes taking place in phosphoric anions one of them leads to the arrangement / configuration of cyclic substances, oligomer or polymeric formation. The analogous compounds are entitled and identified such as cyclophosphates [11-17]. Inorganic polymers' chemistry and technology are one of the main areas of new materials science [18-25]. This area concerns almost all aspects of high technology domains and several scientific works are published in order to study the mentioned field [26-31]. Numerous new inorganic polymers are described in chemical literature for the period of last decades, but a number of the defined entities have not been investigated from a structural point of view to date and the character of the anion remains to be definitively confirmed [2, 4-6]. Built up by a ring of corner-

sharing PO_4 tetrahedral units, the general formula of their anions is $P_nO_{3n}^{n-}$. Actually very interesting anions are known for n=3, 4, 5, 6, 8, 9, 10 and 12 [2-6]. In compliance with the nomenclature published in works [2, 6], the prior groups are: cyclotriphosphates, cyclotetraphosphates, cyclopentaphosphates, cyclohexaphosphates, cyclooctaphosphates, cyclonanophosphates, cyclodecaphosphates, cyclododecaphosphates.

2. MATERIALS AND METHODS

Condensed phosphates (or that is to say inorganic polymers) of polyvalent metals, notably double condensed phosphates of polyvalent metals, also several cyclophosphates with different formula were obtained by diverse methods: by solid phase synthesis, from solution-melts of phosphoric acids etc. Our group of researchers has been working on inorganic synthesis using an environment-friendly method – the knowhow for used chemicals which are decreased wastes with a minimum harm and not producing damaging outputs. In recent years in our previous works we informed about our studies in the open systems M^I_2O–$M^{III}_2O_3$-P_2O_5-H_2O between temperature range 150-500°C, where M^I –Li, Na, K, Rb, Cs and Ag; M^{III}–Ga, In, Sc and in some cases – Al. Analysing various experiments, we revealed the existence of the many double condensed compounds – in fact a series of a formerly new class of inorganic polymers. The method of synthesis of double phosphates from solution-melts of phosphoric acids was applied in the course of our experiments. We have established the best crystallization areas / regions of various condensed phosphates of mono- and polyvalent metals and the greatest temperature ranges for obtaining of one or another pre-planned compounds.

Materials: The initial materials were as follows: ortho-phosphoric acid (85%), carbonates of alkali metals, in some cases - nitrate of silver, oxides of trivalent metals $M^{III}_2O_3$ (where M^{III} was Ga, In, Sc and occasionally – Al). The molar ratio of initial compounds was following: P_2O_5: M^I_2O: $M^{III}_2O_3$ = 15.0: 2.5: 1.0; 15.0: 5.0: 1.0; 15.0:7.5: 1. 0;15.0: 10.0: 1.0. Sometimes we have changed the initial ratio and the following proportion was taken - 15.0 : 3.5 : 1.5; 15.0 : 5.0 : 1.5 ; 15.0 : 6.0 : 1.5; 15.0 : 7.5 : 1.5; 15.0 : 8.5 : 1.5; 15.0 : 12 : 1.5. Every so often the additional volume of phosphoric acid was added during some experiments (for example, sometimes molar ratio 18.0: 8.5: 1.5; 19.0: 10.0:1.5 was taken). In glassy carbon crucible there were mixed gallium oxide, or scandium oxide, or indium oxide, ortho - phosphoric acid (percentage: 85%), nitrate of silver and/or carbonates of alkali metals in various molar ratio.

Methods: At the mentioned temperature range: 100-600 °C we have synthesized several double condensed phosphates. It is acknowledged that sufficient stability of polymeric phosphates makes it able to identify and classify them by the method of paper chromatography. This method together with the chemical analysis, IR spectroscopy, thermo gravimetric analysis, X-ray diffraction analysis, structural analysis was used by us to study the process of formation and composition of many normal, basic and/or acid of both simple and double di-, tri-, tetra-, octa- and dodecaphosphates or ultra-

phosphates of polyvalent metals. Condensed phosphates so obtained were examined by thermogravimetric analysis (TGA). A Q1500-D Derivatograph with a heating rate of 10 degree/min. was used by us (in air atmosphere). In addition to the above were carried out examination using the scanning electronic microscope of the company JEOL (Japan), equipped with a scanning electronic microscope JSM-6510LV. Electronic micrographs was taken by means of reflected (BES) and as well as secondary (SEI) electrons at an accelerating voltage (at 20 kV, the working distance 15 mm). Micro-spectroscopic analysis was performed from the sampling point zones and its surface area.

3. RESULTS AND DISCUSSION

In the systems $M^{I}_2O–M^{III}_2O_3$-P_2O_5-H_2O at the temperature range 150-200 (220) °C the most stable phases are the double triphosphates and /or double dihydrophosphates and/or double triphosphates with the general formulas $M^{I}M^{III}HP_3O_{10}$; $M^{I}M^{III}(H_2P_2O_7)_2$; $M^{I}_2M^{III}P_3O_{10}$. The composition of compounds is in correlation with the initial ratio of components (Figures 1, 2).

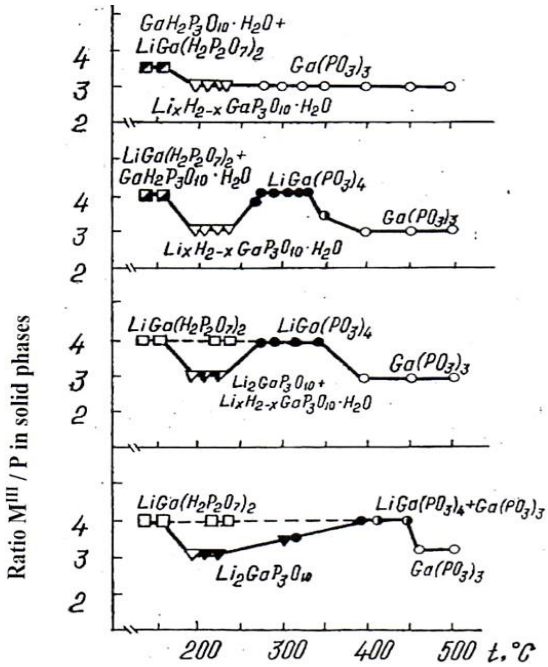

Figure 1: Areas of crystallization of double condensed phosphates of lithium-gallium at temperature range 100-600°C.

Generally, at the temperature range 280-350 °C the most constant phases are the double long chain polyphosphates $[M^{I}M^{III}(PO_3)_4]_x$, obtained in the systems, containing lithium with trivalent metals such as $LiM^{III}(PO_3)_4$,, cyclotetraphosphates $NaM^{III}(PO_3)_4$ or otherwise $NaM^{III}P_4O_{12}$ (obtained for systems, comprising sodium with trivalent metals and / or silver with trivalent metals), cyclooctaphospahates $M^{I}M^{III}(PO_3)_4$ or otherwise $M^{I}_2M^{III}_2P_8O_{24}$ (obtained for systems, containing potassium with Ga, In, and also obtained for rubidium-comprising systems, with Ga and In, for example $K_2Ga_2P_8O_{24}$ and $Rb_2Ga_2P_8O_{24}$.). The configuration of mentioned compounds is in

correspondence with the initial ratio of components and directly, very much depends from temperature of synthesis (Tables 1a, 1b, 2a, 2b, 3). In the same temperature interval 300-355(365) °C for the systems Ag_2O-Ga_2O_3-P_2O_5 and Ag_2O-In_2O_3-P_2O_5 silver forms double cyclotetraphosphates of gallium-silver and indium-silver.

Table 1a. Systems containing K – Ga and K – In: the correlation of the composition of compounds between the initial ratio of components and temperature of synthesis

t, °C	n=5,0	n=7,5	n=10,0	n=5,0	n=7,5	n=10,0
150	$KGa(H_2P_2O_7)$				$KIn(H_2P_2O_7)_2$	
175						
200						
250	$KGaHP_3O_{10}$	$KGaHP_3O_{10}$	$KGaP_2O_7$			
280						
300						
315	$KGa(PO_3)_4$					
350						
380				$In(PO_3)_4$—„C“	$KInP_2O_7$	
400						
420	$Ga(PO_3)_3$—„C“	$KGa(PO_3)_4$				
450						
500						$KInP_2O_7+In(PO_3)_3$

Table 1b. System containing K – Sc: the correlation of the composition of compounds between the initial ratio and temperature of synthesis

t, °C	n=5,0	n=10,0
150		
175		
200	$KSc(H_2P_2O_7)_2$	
250		
260		Mixed phases !
300	$Sc(PO_3)_3$—„C“	$KSc(PO_3)_4$*+$KScHP_3O_{10}$
380		
400		
415		$K_2ScP_3O_{10}$
420	$Sc(PO_3)_3$—„C'“	
500		$KScP_2O_7$
510		

Table 2a. Systems containing Na – Ga and Na – In: the correlation of the composition of compounds between the initial ratio of components and temperature of synthesis

t, °C	n=5,0	n=10,0	n=5,0	n=10,0
150 175 200	$NaGa(H_2P_2O_7)_2$	$NaGa(H_2P_2O_7)_2+NaGaHP_3O_{10}$	$NaIn(H_2P_2O_7)_2$	
270 280 300	$NaGa(PO_3)_4$	$NaGa(PO_3)_4$	$NaIn(PO_3)_4$	$NaInP_2O_7$
350 400 450 500	$Ga(PO_3)_3$—„C“	$NaGaP_2O_7$	$In(PO_3)_3$—„C“	$NaInP_2O_7 + In(PO_3)_3$

Investigation of the systems with scandium and sodium show that the most stable phases are triphosphates (Table 2b). At the temperature range 350-410 °C is synthesized the double ultraphosphate of sodium-scandium $Na_3ScP_8O_{23}$.

Table 2b. System containing Na – Sc: the correlation of the composition of compounds between the initial ratio of components and temperature of synthesis

t, °C	n=5,0	n=10,0
150 175 200	$NaSc(H_2P_2O_7)_2$	
250 280 300	$NaScHP_3O_{10}$	$Na_2ScP_3O_{10}$ $Na_2ScP_3O_{10}+NaScP_2O_7$
350 400 410	$Sc(PO_3)_3 \div Na_3ScP_8O_{23}$	$Na_3ScP_8O_{23}$
450 500	$Sc(PO_3)_3$—„C“	$NaScP_2O_7$

In aim to search some new condensed compounds as well as to study the impact of trivalent and monovalent cations on the formation of inorganic polymers' anionic radical and the level of condensation, we have studied multicomponent systems containing other monovalent and trivalent metals. We have done systematic study of systems M_2^IO-$M_2^{III}O_3$-P_2O_5-H_2O in which M^I is silver and M^{III} – Ga, In, Sc. In the Figure 2 are shown crystal phases obtained in the systems, containing lithium, potassium and as trivalent metal-scandium. The interdependence of the structure of composites from molar ratio of initial components vs temperature is explored.

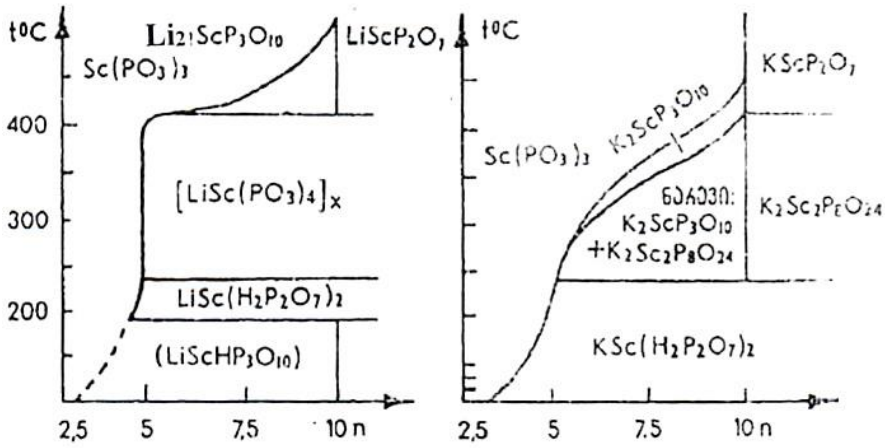

Figure 2. Systems containing lithium, potassium and as trivalent metal-scandium: the interdependence of the composition and the ratio of initial components vs temperature

The double oligo-, and cyclophosphates of alkali metals and silver with abovementioned trivalent metals are primarily synthesized and firstly examined by us. General dependency of structural composition and stability of double condensed phosphates from ion radius of M^{1} - $M^{III}$are also examined. In the Table 3 are presented more interesting synthesized compounds during investigation of systems, containing all alkali metals and scandium.

Table 3: Synthesized compounds, containing all alkali metals and Sc

Double acidic Triphosphates $M^{I}M^{III}HP_3O_{10}$ $M^{III}H_2P_3O_{10}$	**Double Triphosphates** $M^{I}_2M^{III}P_3O_{10}$	**Double acidic Diphosphates (Hydrated)** $M^{I}M^{III}(H_2P_2O_7)_2 \cdot 2H_2O$
Complex Diphosphates $M^{I}_2M^{III}H_3(P_2O_7)_2$	**Double Dihydrophosphates** $M^{I}M^{III}(H_2P_2O_7)_2$	**Double Diphosphates** $M^{I}M^{III}P_2O_7$
Cyclotetraphosphates $M^{I}M^{III}(PO_3)_4]_4$	**Cyclooctaphosphate** $M^{I}_2M^{III}_2P_80_{24}$	**Double Cyclododecaphophates** $M^{I}_3M^{III}_3P_{12}0_{36}$
U l t r	**Polyphosphates** $[M^{I}M^{III}(PO_3)_4]_x$	**Various Polyphosphates** $M^{III}(PO_3)_3$ - (A, C, C^{I} forms)

Investigation of the systems Ag_2O-M^{III}-P_2O_5-H_2O shown crystallization of various new inorganic polymers (Table 4). In the temperature interval 300-355(365) °C for the systems Ag_2O-Ga_2O_3-P_2O_5-H_2O and Ag_2O-In_2O_3-P_2O_5-H_2O silver forms double cyclotetraphosphates of gallium-silver and indium-silver (Table 4). For scandium was obtained cyclododecaphosphate of Sc-Ag (duration of condensation process – 15-18 days).

Table 4: Various newly synthesized condensed phosphates of silver and trivalent metals

$M^IM^{III}(H_2P_2O_7)_2$ **Double acidic diphosphates**	$M^IM^{III}P_2O_7$ **Double diphosphates**	$M^IM^{III}HP_3O_{10}$ **Double acidic triphosphates**	$M^IM^{III}(PO_3)_4$ **Poly - (a), cyclotetra-(b), cyclododeca-phosphates (c)**	$M^{III}(PO_3)_3$ **Polyphosphate forms A and C, C^I**
$Ag(H_2P_2O_7)_2$+ $AgHScP_3O_{10}$	$AgScP_2O_7$	$AgHScP_3O_{10}$	$Ag_3Sc_3P_{12}O_{36}$ (c)	$Sc^{III}(PO_3)_3$
$AgSc(H_2P_2O_7)_2 \cdot H_2O$	$AgGaP_2O_7$		$AgScP_4O_{12}$ (b)	
$Ag(H_2P_2O_7)_2$+ $AgHGaP3O_{10}$	$AgInP_2O_7$		$AgGaP_4O_{12}$ (b)	$Ga^{III}(PO_3)_3$
$AgHInO_{10}$			$AgInP_4O_{12}$ (b)	$In^{III}(PO_3)_3$

During detailed investigation of the systems, containing caesium and trivalent metals, one of the first representatives of the cyclic dodecaphosphates class were synthesized by us as well, with following formulas $Cs_3Ga_3P_{12}0_{36}$, $Cs_3Sc_3P_{12}0_{36}$, $Cs_3In_3P_{12}0_{36}$. The molar ratio for $P/M^I/M^{III}$ was very variable: 15/2.5/1; 15/3.5/1; 15/5.0/1; 15/6.0/1; 15/7.5/1; 15/10.0/1; And sometimes as well: 15/2.5/1.5; 15/3.5/1.5; 15/5.0/1.5; 15/6.0/1.5; 15/7.5/1.5; 15/10.0/1.5 as well as: 18/2.5/1.5; 18/3.5/1.5; 18/5/0/1.5; 18/6.0/1.5; 18/7.5/1.5; 18/10.0/1.5.

Figure 3 shown areas of crystallization of crystalline phosphates and /or double condensed oligo- and cyclic compounds during systematic studies of the systems, containing cesium and gallium and reveal the dependency of structures vs initial ratio of components and temperature range of synthesis.

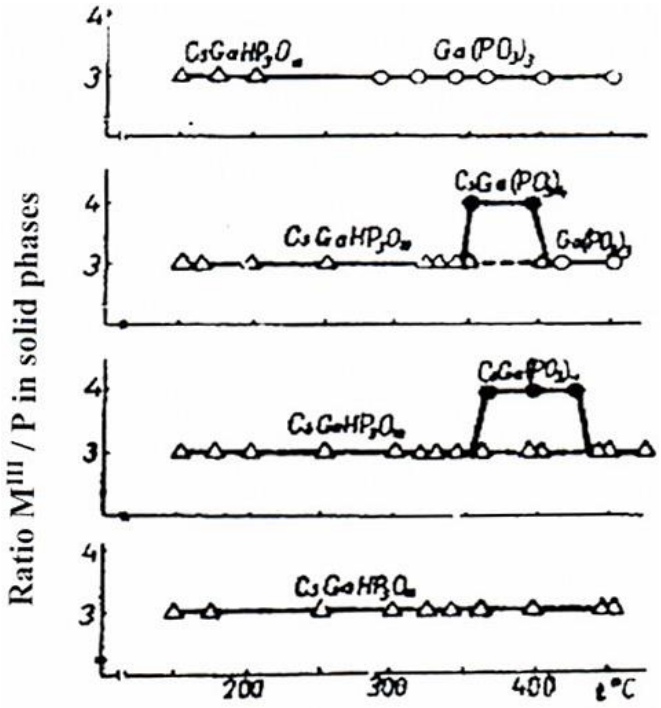

Figure 3. Areas of crystallization of phosphates in the systems, containing cesium and gallium and dependency of the structures vs initial ratio and temperature range

Throughout detailed and systematic investigation of the systems, containing as monovalent metal - silver, one of the first representatives of the double cyclic tetraphosphate of sivler and trivalent metals were synthesized by us as well, with following formula$AgGaP_40_{12}$ and $AgInP_40_{12}$. Pending the best results the molarratio for $P/M^I/M^{III}$was very variable: 15/2.5/1; 15/3.5/1; 15/5.0/1; 15/6.0/1; 15/7.5/1; 15/10.0/1; Similarly with above cases the following proportion was also taken: 15/2.5/1.5; 15/3.5/1.5; 15/5.0/1.5; 15/6.0/1.5; 15/7.5/1.5; 15/10.0/1.5 as well as: 18/2.5/1.5; 18/3.5/1.5; 18/5/0/1.5; 18/6.0/1.5; 18/7.5/1.5; 18/10.0/1.5. We would like to emphasize that in the case of molar ratio n=5 at temperature310-355°C and duration of experiment approximately 12-15 days is obtained cyclic dodecaphosphate of gallium-silver and scandium-silver $Ag_3Sc_3P_{12}\ 0_{36}$, $Ag_3Ga_3P_{12}0_{36}$. At molar ratio 7.5 on the same temperature and duration of synthesis 2-3 days (really in almost similar conditions) the basic phase was the double tetraphosphate of gallium-silver $AgGaP_40_{12}$, withthe small part of$Ag_3Ga_3P_{12}\ 0_{36}$ (as impurityphase). In the Figure 4 are presented the structure of synthesized by us earlier cyclododecaphosphate of cesium-gallium on the plane ***xy*** and polyhedrons of metals [2, 4]. The long-chain polyphosphates of trivalent metals $M^{III}\ (P0_3)_3$ – specifically forms C^I and /or C – are synthesized and studied.

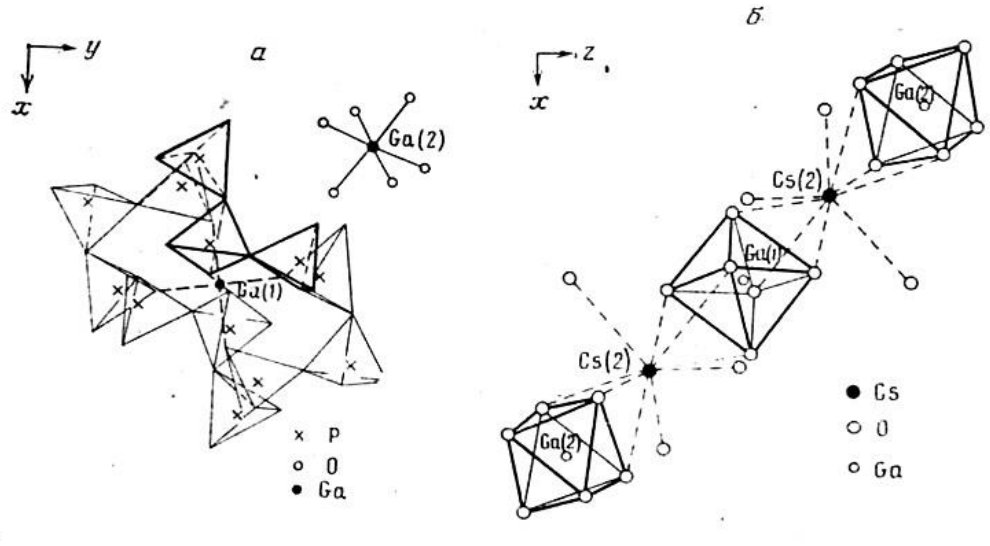

Figure 4. The structure of cyclododecaphosphate of cesium-gallium on the plane xy and the polyhedrons of metals.

This structure is similar with compound of vanadium-cesium $Cs_3V_3P_{12}O_{36}$. A VO_6 octahedron is inserted at the center of the ring [4-5, 2]. In our previous works we have reporting about the data of roentgen phase's analysis and on essential outcomes of obtained by us new condensed phosphates [12, 4-5]. For more informativeness in the proposed work, we included one of the micrographs, obtained for the cyclic condensed gallium-silver compound synthesized at 345-355 °C. In the Figures 5(a) and 5(b) are presented microphotographs, resulting the roentgen-spectral examination of obtained mono crystals by scanning electronic microscope at various enlargements.

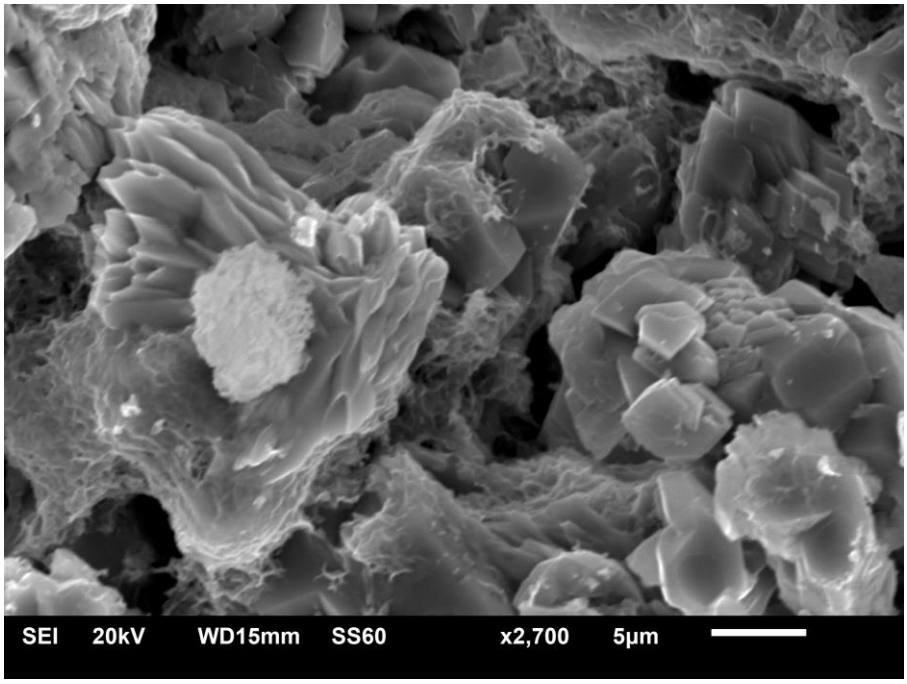

Figure 5a. Electron image for cyclic compound of Ga-Ag, obtained at 335-345°C, n=5.

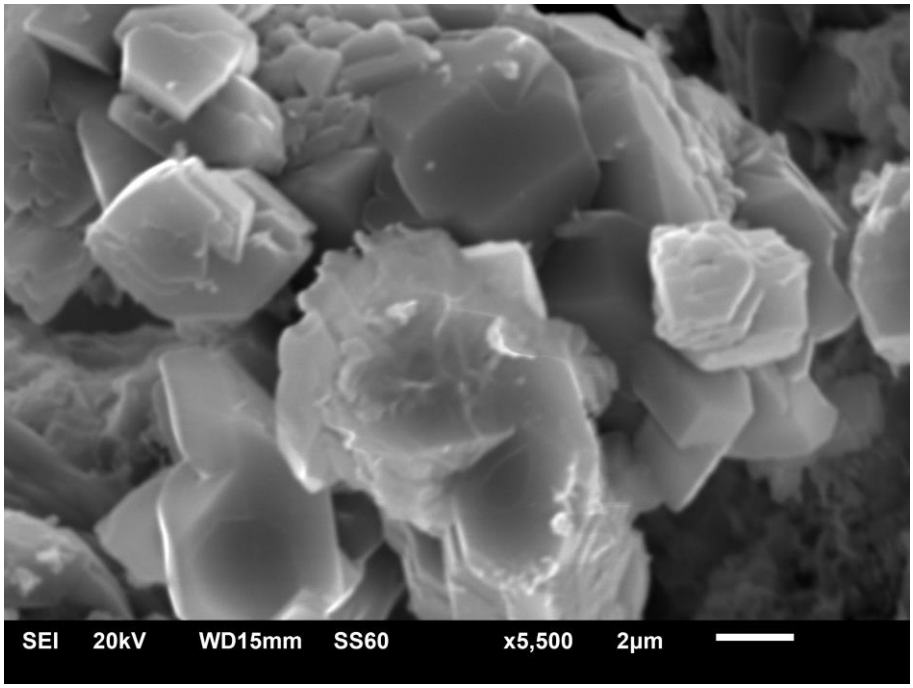

Figure 5b. Electron image for cyclic compound of gallium-silver, obtained at 335-345°C, for initial molar ratio n=5 (at different enlargement).

Thermogravimetric investigation of the acidic double condensed triphosphate of potassium-scandium $KScHP_3O_{10}$ obtained at temperature range 155 °C-350 °C and molar ratio $K_2O : Sc_2O_3$ = 5 (and /or 6.0; 6;5) was revealed two endothermic effects: I at temperature 240 – 300 °C, which corresponds to the elimination of crystallization water and II - at 380-420 °C, which apparently corresponds to the detachment of chemically allied water (mass loss at mentioned temperatures see in Figure 6). The III effect at 560 – 590 °C links to the melting process of tetraphosphate according to the scheme (a).

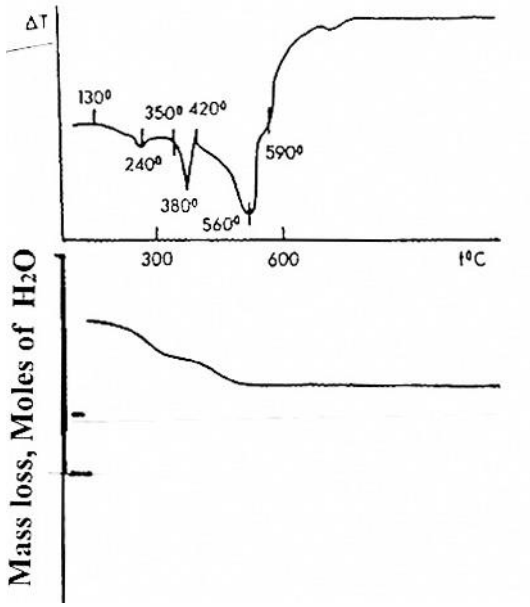

Figure 6. Thermogram of $KScHP_3O_{10}\cdot(0.5–2.0)H_2O$.

After decomposition of mentioned triphosphate two compound: cyclotetraphosphate and diphosphate of potassium-scandium appears, see scheme (a):

$$\mathbf{2KScHP_3O_{10}\cdot 0.5H_20} \xrightarrow{-2H_2O} \mathbf{KScP_4O_{12} + KScP_2O_7} \quad \text{(a)}$$

The examination of the acidic double diphosphate of scandium – rubidium $RbSc(H_2P_2O_7)_2$ (Figure 7) synthesized at 135 – 250 °C at the molar ratio $Rb_2O : Sc_2O_3$= 7.5 (and/or 8–10) prove the evidence of the decomposition by the scheme (b):

$$\mathbf{RbSc(H_2P_2O_7)_2} \xrightarrow{-2H_2O} \mathbf{RbScP_4O_{12}} \quad \text{(b)}$$

The visible loss of mass revealed at the 180-230-270 °C temperature interval corresponding to the thermal transformation and decomposition of the double condensed dihydrophosphate of rubidium-scandium, following which is formed the new compound – cyclotetraphosphate $RbScP_4O_{12}$ (Figure 7).

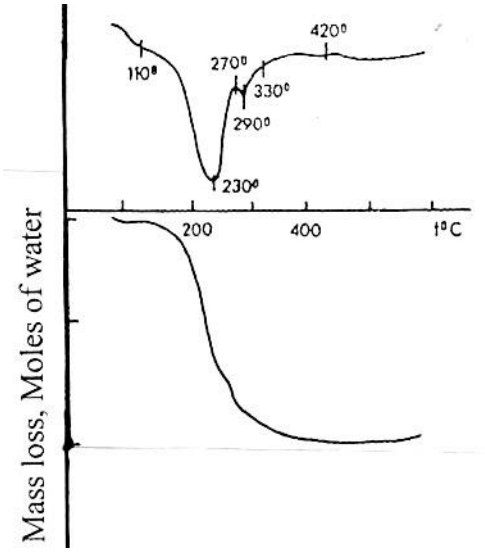

Figure 7. Thermogram of the acidic diphosphate of rubidium-scandium $RbSc(H_2P_2O_7)_2$.

About application of condensed compounds, so called inorganic polymers: the spheres of application of condensed phosphates are very variable, such as: raw materials for creation of phosphates glasses, thermo-resistant materials, effective applying fertilizers, detergents, cement substances, ion-exchange materials and also catalytic agents [3, 5, 7-9]. The composition and thermal properties, as well as the vibrational and luminescent properties of compounds determine their use in quantum electronics. The bio-materials appears on the base of hydroxyl-apatite and polyphosphates. Various important studies are focused on double, triple, polymeric and cyclic phosphates, where oxygen's atoms are interchange by nitrogen, fluorine and sulphur's atoms [3]. Based on the founded and pursuant literary data we can conclude that the dynamic development of phosphate's chemistry during the last years is owing to the explorations and valuable progress in this domain [3-4, 18-25]. Naturally, we should not forget that the obtaining of a new compounds with the mixed anions, notably: phosphate-borates, phosphate-silicates and phosphates, in which the

part of oxygen atoms are replaced by nitrogen, fluorine or sulphur atoms also are well appreciated. The phosphate's binding agents, phosphato-binders and laser materials are supplanted/ replaced by biomaterials, on the base of polyphosphates and hydroxyl apatite. It's been a long time since academician Tananaev always underlined the vital role of hydroxyl apatite, such as main corposant of the bio organisms comparable by their great importance with the DNA [17]. Inorganic polymers' chemistry domain concerns almost every aspect of the high-technology area and its various application touches the contemporary life, from electronics to construction, food and medicine. We would like to accentuate that inorganic polymers' chemistry and technology are one of the main areas of new materials science [27-34]. New polymeric materials, owing of their thermal stability and flexibility, are used as elastomers, fibers, films, to name but a few [28, 30]. It is necessary to emphasize the importance of compounds with structural diversity, including promising systems with a variety of applications – inorganic-organic hybrid materials [31]. Application of phosphates is very huge and cannot be exposed in one paper. The further investigations of this branch of applied chemistry must be interesting for researchers in this domain, especially in purpose to enlarge the sphere of application of condensed phosphates in medicine and various branches of modern life.

4. CONCLUSION

The crystalline new inorganic polymers – condensed phosphates formation in the systems $M_2^IO - M_2^{III}O_3 - P_2O_5 - H_2O$ was investigated. The synthesis process was conducted at temperature range 100-600 °C. Structural arrangement of synthesized double condensed phosphates' are investigated also. Obtained crystalline phases are studied in conjunction with the chemical analysis, by IR spectroscopy, thermo gravimetric analysis, X-Ray diffraction analysis, roentgen-spectral investigation using a scanning electronic microscope. Appropriate data as well as characteristics for synthesized crystalline compounds so called inorganic oligomers and polymers are provided.

In total, more than 80 new condensed compounds were synthesized ; among them should be noted the double ultra-phosphate $M^I_3M^{III}P_8O_{23}$, various double cyclic tetraphosphates with the general formulas $M^IM^{III}P_4O_{12}$, double cyclic octaphosphates $M^I_2M_2{}^{III}P_80_{24}$, cyclic double dodecaphosphates $M^I_3M^{III}_3P_{12}0_{36}$. The long chain polyphosphates M^{III} $(P0_3)_3$ – (forms A and / or C, C^I) are synthesized and studied as well.

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CONFLICT OF INTEREST

There is no financial interest or any conflict of interest.

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