

Areas of crystallization of double condensed phosphates of Ag and trivalent metals and regularities of their formation

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INTRODUCTION

Beginning from the innovator works of scientists a lot of number of condensed compounds, in fact – inorganic polymers was synthesised in the world. A great number of researches in XX Century are really valuable and was appreciated. Among a varieties of processes of condensation of phosphoric anions one of them leads to the prearrangement of cyclic, oligomeric or polymeric structures of condensed phosphates. Domain of condensed phosphates advanced much rapidly, for the causes of the development of advanced methods of analysis and of the important application of phosphates materials in several technical field, including nanotechnologies. The chemistry of inorganic compounds of phosphorous has advanced intensively in the last time also for the purpose that condensed compounds of phosphorus are greatest applicable, useful and convenient for promote development of the chemistry of inorganic polymers, and last but not least - they are reasonably presumed as best fertilizers, detergents and as materials used in engineering, construction and other areas, such as raw materials for creation of glasses, thermo-resistant constituents, effective applying nourishments, cleaners, cement substances, ion-exchange ingredients and also catalytic agents. The composition and thermal properties, as well as the vibrational and luminescent properties of condensed compounds determine their use in quantum electronics. The bio-materials appears on the base of hydroxiapatite and polyphosphates much rapidly.

Objectives / Methods of analysis

In aim to search for new condensed compounds as well as to study the impact of trivalent and monovalent cations for the formation of inorganic polymer's anionic radicals and the level of condensation, we have studied multicomponent systems containing monovalent and trivalent metals: $M_2^I O - M_2^{III} O_3 - P_2 O_5 - H_2 O$ at 130-550 °C (which M^I is Ag, M^{III} – Ga, In and Sc). General dependency of structural composition and stability of double condensed phosphates from ion radius of M^I – are also examined. The double oligo-, and cyclophosphates are primarily synthesized and firstly examined by us. Synthesized compounds are investigated and were detailed examined / identified by X-Ray phase's analysis, paper chromatography, and thermogravimetric analysis. The electron microscope scan was performed on a Japanese electron scanning microscope JSM-6510LV, which was equipped with an energy dispersive X-Max^N 20 analyzer (by Oxford Instrument). Micrographs were taken at various extension both from point areas, and from a certain surface.

Materials

In glassy- carbon crucible there were mixed gallium oxide, or scandium oxide, or indium oxide, orthophosphoric acid (percentage: 85%) and nitrate of silver in various molar ratio. The offered data are the outcomes of synthesis by crystallization from melts of polyphosphoric acids during investigation of multi-component systems containing in addition to alkali metals another monovalent metal - Silver (Ag) and such as Ga, In, Sc. The molar ratio $P_2 O_5 : M_2^I O : M_2^{III} O_3$ are also slightly changed $P_2 O_5 : M_2^I O : M_2^{III} O_3 = 15:2,5:1,0; 15:5:1,0; 15:7,5:1,0$ and $15:3,5:1,5; 15 :5 :1,5 ; 15:6:1,5; 15 :7,5 :1,5 ;15:8,5:1,5; 15:12:1,5$.

EXPERIMENTAL

Various experiments revealed that by crystallization from melts of polyphosphoric acids were obtained the following double condensed compounds – namely a series of an formerly new class of inorganic polymers : double condensed di- and triphosphates, cyclotetraphosphates, Analyzing the experimental data shows that we obtained the following condensed phosphates: acidic di- and triphosphates of Ga, In and Sc with silver $AgSc(H_2P_2O_7)_2$, $Ag_2ScH_3(H_2P_2O_7)$ and $AgScHP_3O_{10}$ at the temperature range 140-230°C and on molar ratio $Ag_2O:Sc_2O_3=5$ (6,0; 6,5; 7,5). The increase of temperature approximately to 260-340°C-leads to the formation of double cyclotetraphosphates $AgGaP_4O_{12}$; $AgInP_4O_{12}$; $AgScP_4O_{12}$ on molar ratio $Ag_2O:Sc_2O_3=5,0; 6,0; 6,5; 7,5$. At relatively high temperatures the polyphosphates are obtained according to the general formula $(M^{III}PO_3)_3$.

Results

In fact the systems, containing Ag-Sc needs to be thoroughly explored at temperature range 620-850K in more depth which is the objective of our study at present time. It should be noted that we also received double condensed phosphate – cyclododecaphosphate of Gallium-Silver $Ag_3Ga_3P_{12}O_{36}$. It crystallizes with an impurity second phase at temperature range 605-615K (molar ratio P/Ag/Ga=18/5/1,3), duration of synthesis – 3-4 days. By our opinion in the future it is necessary to carefully select other molar ratios and the continuity of the synthesis to obtain a pure phase. Phase formation in system and the microstructure of synthesized double condensed phosphates [...] are investigated by X-Ray diffraction analyses (data summarized in tables 3 and 4). The powder diffraction data for cited compounds, intensity data collections are obtained on diffractometer DRON-3M, anodic Cu-K α radiation, the range $2\theta=10^0-60^0$, detector's speed 2⁰/min., lattice spacing d_n/n in Angströms Å, and I/I_0 – it is relative intensity (used model/ standard data – by American Society for Testing and Materials – ASTM) Detailed comparison with our previously obtained XRD data for similar compounds of Gallium, Indium and Scandium are also carried out /performed. On the assumption of the fact that combinations of cations (Ag-Ga, Ag-In and Ag-Sc) for cyclophosphates have not been studied and hence are not given in the file index (typical XRD data), roentgenograms was compared to our standard data models, to similar compounds of Ag-P and our standard data prototypes for similar double condensed phosphates of Gallium, Indium, Scandium with alkali metals [7-13]. We perform, that any initial components: M_2CO_3 , Sc_2O_3 , $AgNO_3$ are already completely irreversibly interreacted during synthesis process. Below are presented synthesized compounds.

$M^I M^{III} (H_2P_2O_7)_2$	$M^I M^{III} P_2O_7$	$M^I M^{III} HP_3O_{10}$	$M_2^I M^{III} P_3O_{10}$	$M^I M^{III} (PO_3)_4$	$M^{III} (PO_3)_3$
$LiSc(H_2P_2O_7)_2$	$LiScP_2O_7$	$LiScHP_3O_{10}$	$Li_2ScP_3O_{10}$	$\{LiSc(PO_3)_4\}_x$	$Sc(PO_3)_3$ -A
$NaSc(H_2P_2O_7)_2$ + mix phases	$NaScP_2O_7$	$NaScHP_3O_{10}$	$Na_2ScP_3O_{10}$	$Na_3ScP_8O_{23}$ ultra phosphate	$Sc(PO_3)_3$ -C
$KSc(H_2P_2O_7)_2$	$KScP_2O_7$	$KScHP_3O_{10}$	$K_2ScP_3O_{10}$	$K_2Sc_2P_8O_{24}$	
$RbSc(H_2P_2O_7)_2$	$RbScP_2O_7$	$RbScHP_3O_{10}$	$Rb_2ScP_3O_{10}$	$Rb_2Sc_2P_8O_{24}$	
$CsSc(H_2P_2O_7)_2$	$CsScP_2O_7$	$CsScHP_3O_{10}$	$Cs_2ScP_3O_{10}$	$Cs_3Sc_3P_{12}O_{36}$	
$AgSc(H_2P_2O_7)_2$ + $AgHScP_3O_{10}$ Mix phases	$AgScP_2O_7$	$AgHScP_3O_{10}$			
$AgSc(H_2P_2O_7)_2 \cdot H_2O$				$AgScP_4O_{12}$	
				$AgGaP_4O_{12}$	
				$AgInP_4O_{12}$	

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Classes of Synthesized Phosphates by us

Doubles acidic Triphosphates $M^I M^{III} HP_3O_{10}$ or $M^{III} H_2 P_3 O_{10}$	Double Triphosphates $M^I_2 M^{III} P_3 O_{10}$	Double acidic Diphosphates (Hydrated) $M^I M^{III} (H_2 P_2 O_7)_2 \cdot 2H_2 O$
Complex Diphosphates $M^I_2 M^{III} H_3 (P_2 O_7)_2$	Double Dihydrophosphates $M^I M^{III} (H_2 P_2 O_7)_2$	Double Diphosphates $M^I M^{III} P_2 O_7$
Double Cyclotetraphosphates $M^I M^{III} (PO_3)_4$	Double Cyclooctaphosphates $M^I_2 M_2^{III} P_8 O_{24}$	Double Cyclododecaphosphates $M^I_3 M_3^{III} P_{12} O_{36}$
Ultraposphates $M^I_3 M^{III} P_8 O_{23}$	Long Chain Double Polyphosphates $[M^I M^{III} (PO_3)_4]_x$	Various Polyphosphates $M^{III} (PO_3)_3$ - (A, C etc. forms)

Conclusions

At relatively low temperatures it is more probably to produce double acidic phosphates, with increasing synthesis temperature double tetraphosphates are formed which are isomorphs among themselves and which are isostructural with the sodium-gallium double condensed tetraphosphates. Via comparison of the obtained condensed compounds with appropriate phosphates, synthesized by us earlier (in the systems containing Ga, In and Sc, it is possible to conclude that while the radius of trivalent metal decreases, the polyphosphate chain identity period upsurges. The less of the correlation / ratio, greater is the possibility of big cycle formation, for exemple for obtaining of cycloocta- or cyclododecaphosphates. The optimum achievement for the production of the great cyclic anions is parity of the big cations of monovalent metal versus trivalent metals with small ionic radius.

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