



CRYSTALLIZATION FIELDS OF CONDENSED SCANDIUM-SILVER AND GALLIUM-SILVER PHOSPHATES

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We have been able to synthesize a diverse new group of condensed phosphate polymers in the systems $\text{Me}^{\text{I}}_2\text{O}-\text{Me}^{\text{III}}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ (where Me^{I} represents Ag, Na, Cs, and Me^{III} represents gallium, scandium and indium. The structural arrangement of synthesized condensed phosphates is ascertained using X-ray spectral analysis, X-ray diffraction and IR spectroscopy. An interesting approach to the synthesis of double compounds containing Ga, In, Sc and monovalent metals, including Ag, resulting in the production of double phosphates is described.

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Introduction

The development of nanotechnologies for obtaining of inorganic phosphate polymers, notably – double condensed phosphates of polyvalent metals – as well as the study of their crystallization fields is a topical task. There are many research topics devoted to this subject,¹⁻¹¹ especially those aimed at determining the conditions for producing some new condensed phosphates of polyvalent and monovalent cations including alkaline metals.⁸⁻¹⁹

The significant advances in the chemistry of inorganic compounds of phosphorous in the past few years are due to new application fields of inorganic phosphate oligomers and polymers.^{7,20-27}

Experimental

We have studied the $\text{Me}^{\text{III}}_2\text{O}_3-\text{Me}^{\text{I}}_2\text{O}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ and systems ($\text{M}^{\text{I}}=\text{Ag, Na, M}^{\text{III}}=\text{Sc, In and Ga}$) at the temperature range of 100–600 °C. This work contains data concerning the synthesis and crystallization fields of certain condensed double phosphates of trivalent and monovalent metals (including, in particular, Ga, In, Sc and monovalent metals, notably Ag), resulting in the production of double phosphates depending on the temperature and molar ratio of the initial components.

The initial components were oxides of gallium, indium and/or scandium, silver nitrate (in some cases – sodium carbonate) and orthophosphoric acid. But when the synthesis temperature range is high enough, we generally present the

studied system as oxides of suitable elements, such as $\text{Me}^{\text{III}}_2\text{O}_3$, Ag_2O and P_2O_5 . The variation of the molar ratio of initial components $n=\text{Ag}/\text{Me}^{\text{III}}$ was very broad: from 1.5 to 10.0, but constant for each experiment – for each temperature range. The molar ratio of phosphorus to trivalent metal was always the same during all synthesis processes and was equal to $n_1=\text{P}/\text{Me}^{\text{III}}=15.5$.

Trivalent metal oxide, orthophosphoric acid (percentage: 85 %) and monovalent metal salt – silver nitrate - were mixed in a glassy carbon crucible at different molar ratios and heated to temperatures between 100 and 600 °C. The duration of the synthesis process was very variable, from 3-5 days to 15-20 days, depending on the temperature of the experiments. The crystals formed in the melts were removed by extraction of 15-20 g samples with 500-700 mL of distilled water.

The condensation degree of the synthesized polymeric phosphates (di-, tri-, tetra-, and/or dodecaphosphates) was checked by paper chromatography. For the chromatographic analysis, the obtained crystalline samples were decomposed with H-form cation type ion-exchanger. In these experiments, 0.1 g of the substance was contacted for ca. 1 h with an aqueous suspension of 2 g (KU-2) type sulfonated cation exchanger at ~0 °C. After the decomposition of the main mass of the substance according to the following scheme: cationite-H(solid) + M-phosphate(solid) → cationite-M(solid)+H-phosphate(liquid) the solution, containing phosphoric acids was neutralized with sodium bicarbonate and chromatographed on Filtrak FN-11 paper (Germany) by acidic $\text{CCl}_3\text{COOH}-\text{CH}_3\text{COOH}-\text{CH}_3\text{OH}$ solvent. Chromatograms were sprayed with ammonium molybdate $(\text{NH}_4)_2\text{MoO}_4$ 5% solution and irradiated with ultraviolet light ($\lambda=400$ nm).

Scanning electronic microscope measurements were performed on a JEOL scanning electronic microscope JSM-6510LV (well-appointed by energy-disperse X-Max N 20 micro-X-ray spectral analyzer produced by Oxford Instruments). SEM measurements were carried out by means of reflected (BES) as well as secondary (SEI) electrons at an accelerating voltage (at 20 kV). The working distance was approximately 15 mm. Micrographs have been taken at the diverse enlargements.

Table 1. Dependence of composition from temperature T and molar ratio $n = \text{Ag}_2\text{O}/\text{Sc}_2\text{O}_3 = 1.5\text{--}2.5, 3.5\text{--}5.0, 6.0\text{--}7.5,$ and $8.0\text{--}10.0$.

$T, ^\circ\text{C}$	$n = 1.5\text{--}2.5$	$n = 3.5\text{--}5.0$	$n = 6.0\text{--}7.5$	$n = 8.0\text{--}10.0$
130 – 150	$\text{Sc}(\text{PO}_3)_3\text{--C}$	$\text{AgScHP}_3\text{O}_{10}$	$\text{AgSc}(\text{H}_2\text{P}_2\text{O}_7)_2$	$\text{AgSc}(\text{H}_2\text{P}_2\text{O}_7)_2$
180 – 200	$\text{Sc}(\text{PO}_3)_3\text{--C}$	$\text{AgScHP}_3\text{O}_{10}$	$\text{AgScHP}_3\text{O}_{10}$	$\text{AgScHP}_3\text{O}_{10}$
220 – 240	$\text{Sc}(\text{PO}_3)_3\text{--C}$	$\text{AgScP}_4\text{O}_{12}$	$\text{AgScP}_4\text{O}_{12}$	$\text{AgScP}_4\text{O}_{12}$
310 – 335	$\text{Sc}(\text{PO}_3)_3\text{--C}^I$	$\text{AgScP}_4\text{O}_{12}, \text{AgScHP}_3\text{O}_{10}$	$\text{AgScP}_4\text{O}_{12}$	$\text{AgScP}_4\text{O}_{12}$
340 – 355	$\text{Sc}(\text{PO}_3)_3\text{--C}^I$	$\text{AgScP}_4\text{O}_{12}$	$\text{AgScP}_4\text{O}_{12} + \text{Ag}_3\text{Ga}_3\text{P}_{12}\text{O}_{36}$	$\text{AgScP}_4\text{O}_{12}$
400 – 450	$\text{Sc}(\text{PO}_3)_3\text{--C}^I$	$\text{AgScHP}_3\text{O}_{10}$	$\text{AgScHP}_3\text{O}_{10}$	$\text{Ag}_2\text{ScP}_3\text{O}_{10}$
500 – 550	$\text{Sc}(\text{PO}_3)_3\text{--C}^I$	$\text{Ag}_2\text{ScP}_3\text{O}_{10}$	$\text{AgScHP}_3\text{O}_{10}, \text{Ag}_2\text{ScP}_3\text{O}_{10}$	AgScP_2O_7

Table 2. XRD data for acid diphosphate $\text{AgSc}(\text{H}_2\text{P}_2\text{O}_7)_2$, acid triphosphate $\text{AgScHP}_3\text{O}_{10}$, tetraphosphates $\text{AgGaP}_4\text{O}_{12}$ and $\text{AgScP}_4\text{O}_{12}$,^{8,10} obtained by us and ASTM–11–642 data for silver triphosphate.

$\text{AgScHP}_3\text{O}_{10}$		$\text{Ag}_3\text{P}_3\text{O}_{10}$ (ASTM–11–642)		$\text{AgSc}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$		$\text{NaSc}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$		$\text{AgScP}_4\text{O}_{12}$		$\text{AgGaP}_4\text{O}_{12}$		$\text{NaGaP}_4\text{O}_{12}$	
d_0/n	I/I_0	d_0/n	I/I_0	d_0/n	I/I_0	d_0/n	I/I_0	d_0/n	I/I_0	d_0/n	I/I_0	d_0/n	I/I_0
–	–	4.81	20	–	–	–	–	4.69	5	4.67	7	4.71	8
4.04	24	–	–	4.04	25	–	–	–	–	4.43	15	4.43	25
–	–	–	–	–	–	4.17	41	–	–	4.20	19	4.27	30
–	–	–	–	–	–	4.00	37	3.94	5	3.94	27	3.94	49
–	–	–	–	–	–	–	–	3.83	100	3.83	80	3.80	15
–	–	3.69	5	–	–	3.67	10	3.63	10	–	–	3.65	8
–	–	3.60	5	–	–	3.59	4	3.56	10	–	–	3.53	5
3.36	–	–	–	3.43	33	3.49	25	–	–	–	–	–	–
–	72	3.37	10	–	–	3.35	29	3.37	31	3.38	38	3.35	16
3.20	–	3.29	10	3.32	24	–	–	–	–	–	–	3.29	5
–	29	3.21	15	–	–	3.24	96	–	–	–	–	3.14	5
3.03	–	3.15	25	3.08	33	3.18	8	–	–	3.08	23	3.08	10
–	9	3.04	15	3.02	30	–	–	3.03	80	3.03	100	3.03	100
–	–	2.96	50	2.98	100	2.98	100	–	–	2.82	18	–	–
2.84	–	–	–	–	–	2.96	19	–	–	2.75	40	–	–
–	100	2.86	95	2.82	55	2.82	52	2.83	19	–	–	2.85	20
–	–	2.76	50	–	–	–	–	2.77	20	2.69	15	2.76	10
–	–	2.72	50	2.74	28	2.74	7	–	–	–	–	–	–
2.64	–	–	–	–	–	2.70	14	2.68	25	2.56	13	–	–
2.59	77	2.60	100	2.64	23	2.62	5	–	–	–	–	2.63	10
2.52	69	–	–	–	–	2.58	4	2.56	15	2.40	19	2.56	3
2.43	14	2.52	30	2.54	32	2.55	7	2.49	16	–	–	2.48	7
2.37	7	2.46	15	–	–	2.47	4	2.41	26	–	–	2.40	3
–	8	2.38	10	–	–	2.39	7	–	–	–	–	–	–
–	–	2.33	5	–	–	2.33	6	2.33	6	2.25	15	2.32	29
–	–	–	–	2.31	32	2.30	4	–	–	–	–	–	–
2.21	–	–	–	2.25	18	–	–	2.25	16	2.15	11	2.20	16
2.13	20	–	–	2.22	18	2.17	12	2.20	12	–	–	–	–
–	31	2.15	5	–	–	–	–	–	–	2.06	6	2.14	5
–	–	2.10	5	–	–	2.10	18	–	–	2.03	5	2.13	3
2.03	–	–	–	2.03	9	2.07	6	2.07	2	–	–	–	–
–	20	2.00	10	–	–	2.04	7	–	–	–	–	2.05	3
1.93	–	1.96	15	–	–	2.02	18	2.00	5	1.89	8	–	–
1.89	11	1.94	5	–	–	1.95	11	1.92	7	–	–	–	–
–	10	1.89	15	–	–	–	–	–	–	–	–	–	–
1.76	–	1.88	10	1.83	21	–	–	1.87	6	1.68	8	1.87	3
1.67	6	–	–	1.75	11	–	–	1.86	6	–	–	1.85	6
1.64	18	–	–	1.68	22	–	–	1.69	6	–	–	–	–
1.62	18	–	–	1.66	28	–	–	–	–	–	–	–	–
–	18	–	–	1.64	33	–	–	–	–	–	–	–	–
–	–	1.59	10	1.57	19	–	–	–	–	–	–	–	–

The powder diffraction intensity data collections were performed on a DRON-3M diffractometer, with anodic Cu- K_{α} radiation in the range of $2\theta = 10-60^{\circ}$, detector's speed $2^{\circ} \text{ min}^{-1}$, lattice spacing d_0/n in Å, and I/I_0 – is the relative intensity (used model/standard data – by American Society for Testing and Materials – ASTM).

The thermal analysis was accomplished by DTA using Q1500-D derivatograph with heating rate of $10^{\circ} \text{ C} / \text{ min}$. in air atmosphere and up to maximal temperature of 1100° C .¹⁰ XRD data of some double condensed phosphates prepared by us, namely acidic diphosphate $\text{AgSc}(\text{H}_2\text{P}_2\text{O}_7)_2$, acidic triphosphate $\text{AgScHP}_3\text{O}_{10}$, tetraphosphates $\text{AgGaP}_4\text{O}_{12}$,

$\text{AgScP}_4\text{O}_{12}$, $\text{NaGaP}_4\text{O}_{12}$ and standard ASTM-11-642 data for silver triphosphate are presented in Table 2. Table 3 contains the XRD data for the double condensed tetraphosphates of silver with gallium and scandium, or sodium and gallium (molar ratio $n=\text{Me}^I/\text{Me}^{III}=7.5$).

The elemental composition of the condensed compounds was examined by gravimetric analysis. Phosphorus was determined by precipitation using a molybdate reagent and a quinoline solution.²⁵ Gallium, indium and scandium were determined by the hydroxyquinoline precipitation method.^{11,25} Silver was determined using argentometry using titration (Volhard) method.²⁸

Table 3. The XRD data for synthesized gallium-silver, gallium-sodium, indium-silver, scandium-silver tetraphosphates (molar ratio $n=\text{Me}^I/\text{Me}^{III}=7.5$).

AgGaP ₄ O ₁₂ (at 335 °C)		AgScP ₄ O ₁₂ (at 335 °C)		NaInP ₄ O ₁₂ (at 335–345 °C)		NaGaP ₄ O ₁₂ (at 335–345 °C)	
d_0/n	I/I_0	d_0/n	I/I_0	d_0/n	I/I_0	d_0/n	I/I_0
4.65	7	4.49	48	4.43	28	4.43	25
4.23	8	4.33	38	4.33	18	4.27	30
4.04	17	3.94	45	3.95	53	3.94	49
–	–	–	–	3.91	98	–	–
3.81	13	3.83	50	–	–	3.80	15
3.63	8	–	–	3.66	16	3.65	8
–	–	3.56	65	–	–	3.53	5
–	–	–	–	3.42	12	–	–
3.39	29	–	–	–	–	–	–
–	–	3.36	39	3.36	15	3.35	16
–	–	–	–	3.27	5	3.29	5
–	–	–	–	3.24	5	–	–
–	–	–	–	3.20	55	–	–
–	–	–	–	3.15	8	3.14	5
–	–	–	–	–	–	3.08	10
3.03	100	3.05	100	3.04	100	3.03	100
–	–	2.89	34	2.93	4	–	–
–	–	2.83	34	2.86	6	2.85	20
2.80	20	2.80	40	–	–	2.76	10
–	–	2.61	16	2.79	22	2.63	10
2.55	15	–	–	–	–	2.56	3
2.50	15	2.49	20	–	–	2.48	7
–	–	–	–	2.46	8	–	–
–	–	–	–	2.45	15	2.40	3
–	–	–	–	2.44	5	2.32	29
2.27	18	–	–	2.32	38	–	–
2.25	22	2.25	25	–	–	–	–
2.23	22	–	–	2.22	4	–	–
2.20	13	2.20	16	–	–	2.20	16
2.07	6	–	–	2.07	8	2.14	5
–	–	2.06	13	–	–	2.13	3
1.95	13	2.01	9	–	–	2.05	3
–	–	1.98	8	1.87	7	1.87	3
–	–	–	–	1.85	38	1.85	6
–	–	1.86	5	1.82	5	–	–
1.78	10	–	–	–	–	–	–
1.75	10	–	–	1.74	14	–	–
1.63	11	1.76	8	1.68	5	–	–
–	–	1.65	13	–	–	–	–
–	–	1.59	9	–	–	–	–

Results and discussion

A series of double condensed phosphate compounds were prepared and assigned during the investigation of systems $\text{Me}^{\text{III}}_2\text{O}_3\text{-Ag}_2\text{O-P}_2\text{O}_5\text{-H}_2\text{O}$ at the temperature interval of 100–600 °C. The phase identity was studied by XRD. The synthesized inorganic polymers containing silver and scandium are presented in Table 1. There are three stable double phosphate phases formed at the temperature range of 130–200 °C depending on the Ag/Sc molar ratio: double acidic diphosphate and triphosphate of scandium and silver, $\text{AgSc}(\text{H}_2\text{P}_2\text{O}_7)_2$, $\text{AgScHP}_3\text{O}_{10}$, respectively, and the double triphosphate, $\text{Ag}_2\text{ScP}_3\text{O}_{10}$.^{8,19} A new silver scandium cyclotetraphosphate ($\text{AgScP}_4\text{O}_{12}$) was synthesized in the temperature interval of 240–340 °C. Analogous compounds could be obtained in similar systems containing Ag-Ga and Ag-In components.

The XRD data of phases obtained at 335–350 °C for the system containing Ga and Ag (molar ratio $n=\text{Me}^{\text{I}}/\text{Me}^{\text{III}}=7.5$) and their comparison with the cesium gallium cyclododecaphosphate²⁵ are presented in Table 4.

Table 4. XRD data of phases obtained in the system containing Ag and Ga at 335–350 (molar ratio $n=\text{Me}^{\text{I}}/\text{Me}^{\text{III}}=7.5$).

$\text{Cs}_3\text{Ga}_3\text{P}_{12}\text{O}_{36}$		$\text{AgGaP}_4\text{O}_{12}+\text{Ag}_3\text{Ga}_3\text{P}_{12}\text{O}_{36}$	
d_a/n	I/I_0	d_a/n	I/I_0
5.09	14	4.69	5
–	–	–	–
4.00	24	3.94	5
–	–	–	–
3.86	100	3.83	100
–	–	–	–
3.59	5	–	–
3.50	20	3.63	10
–	–	3.56	10
3.25	24	3.37	31
3.14	20	–	–
2.94	40	3.03	80
2.83	68	2.83	19
2.76	7	2.77	20
2.68	14	2.68	25
–	–	2.56	15
–	–	2.49	16
2.40	6	2.41	26
2.36	40	2.33	6
2.33	10	2.25	16
2.27	7	2.20	12
2.17	4	–	–
2.14	5	2.07	2
–	–	2.00	5
–	–	1.92	7
–	–	1.87	6
–	–	1.86	6
–	–	1.69	6

The XRD data of similar compounds formed in the analog systems containing gallium and silver, indium and silver and scandium and silver were compared. We ascertain that any of the initial components - trivalent metal oxides, silver nitrate and phosphoric acid completely and irreversibly interact with each other during the synthesis.

The XRD data for the Ag-Sc, Ag-In and Ag-Ga di-, tri-, tetra- or cyclododecaphosphates have been compared with available standard data for analogous double condensed phosphates of trivalent and monovalent (alkali) metals.^{1-9,13,17-20,26} The identification of the obtained crystalline phases was done in accordance with standard ASTM data and based on the results of chemical analyses. The composition of the synthesized compounds prepared was found to be the following: double acidic diphosphates $\text{Me}^{\text{I}}\text{Me}^{\text{III}}(\text{H}_2\text{P}_2\text{O}_7)_2$ and their monohydrates $\text{Me}^{\text{I}}\text{Me}^{\text{III}}(\text{H}_2\text{P}_2\text{O}_7)_2\cdot\text{H}_2\text{O}$, double acidic triphosphates $\text{Me}^{\text{I}}\text{Me}^{\text{III}}\text{HP}_3\text{O}_{10}$, double triphosphates $\text{Me}^{\text{I}}_2\text{Me}^{\text{III}}\text{P}_3\text{O}_{10}$ and cyclotetraphosphates $\text{Me}^{\text{I}}\text{Me}^{\text{III}}\text{P}_4\text{O}_{12}$.

Despite the different ionic radius of Ag and Cs (1.13 and 1.67 Å, respectively) an analog Ag-Ga compound, ($\text{Ag}_3\text{Sc}_3\text{P}_{12}\text{O}_{36}$) was formed as that was synthesized in the Cs-Ga system earlier ($\text{Cs}_3\text{Ga}_3\text{P}_{12}\text{O}_{36}$).²⁵ Based on results of paper chromatography, chemical analysis and XRD analysis, we can conclude that at 335–340 °C and $n=\text{Ag}/\text{Ga}=7.5$, a mixed phase crystallized out with ca. 80 % $\text{Ag}_3\text{Ga}_3\text{P}_{12}\text{O}_{36}$ and ca. 20 % $\text{AgGaP}_4\text{O}_{12}$ content.

The silver scandium cyclotetraphosphate is isostructural with the appropriate silver gallium, silver indium and sodium gallium cyclotetraphosphates, in spite of differences between the ionic radius of sodium and silver (0.98 and 1.13 Å, respectively).

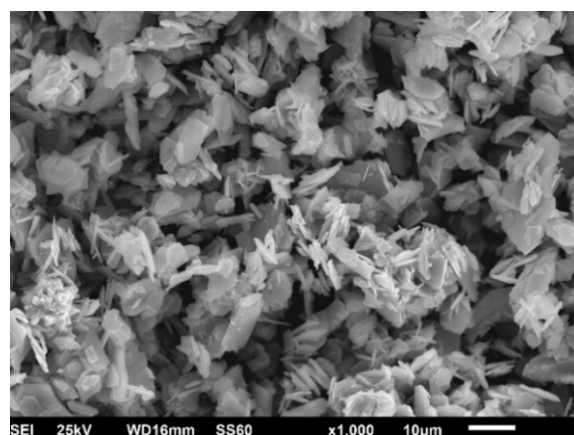


Figure 1. Electron (SEI) image of $\text{AgScHP}_3\text{O}_{10}$ (enlargement 1000).

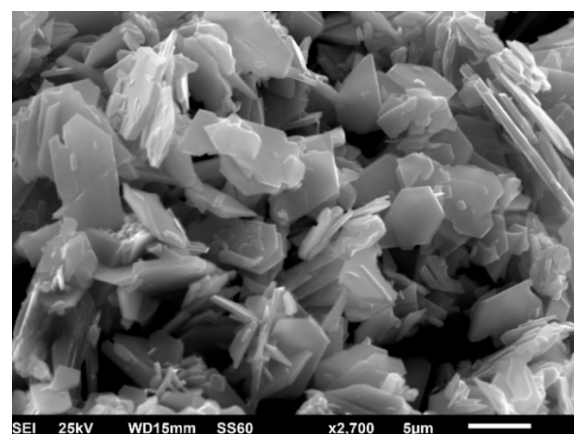


Figure 2. Electron (SEI) image of $\text{AgScHP}_3\text{O}_{10}$ (enlargement 2700).

The EDAX results of silver-scandium double phosphates are presented in Table 5. Figures 1 and 2 illustrate electron images (on enlargements 1000 and 2700 respectively) for silver scandium acidic triphosphate ($\text{AgScHP}_3\text{O}_{10}$). The EDAX spectrum can be seen in Fig. 3. This double compound was obtained at $\text{Ag}/\text{Sc} = 5.0$ at ca. 150°C . Very small crystals of lamellar and needle-like shape with a thickness about of 100 nm were observed.

Figures 4 and 5 show photos for double acidic diphosphate synthesized at the same temperature and molar ratio $\text{Ag}/\text{Sc} = 7.5$.

Table 5 and 6 shows the atomic percentage data vs. spectrum labels for crystals obtained at 335°C in the system containing Ag and Ga for initial ratio $\text{Me}^{\text{I}}/\text{Me}^{\text{III}} = 5.0$.

Table 5. Atomic percentage data vs. spectrum labels for crystals obtained at 335°C in the system containing Ag-Ga, for initial ratio $n = \text{Me}^{\text{I}}/\text{Me}^{\text{III}} = 5.0$.

Atom	Atomic %				Statistics			
	1	2	3	4	Max	Min	Average	Standard deviation
O	73.88	75.83	75.69	75.70	75.83	73.88	75.27	0.93
P	14.86	12.92	12.98	13.02	14.86	12.92	13.45	0.94
Ga	3.61	3.40	3.42	3.38	3.61	3.38	3.45	0.10
Ag	7.65	7.86	7.90	7.90	7.90	7.65	7.83	0.12

The Figures 4-6 represent SEM pictures of obtained crystals of in the $\text{Me}^{\text{III}}_2\text{O}_3\text{-Ag}_2\text{O-P}_2\text{O}_5\text{-H}_2\text{O}$ systems.

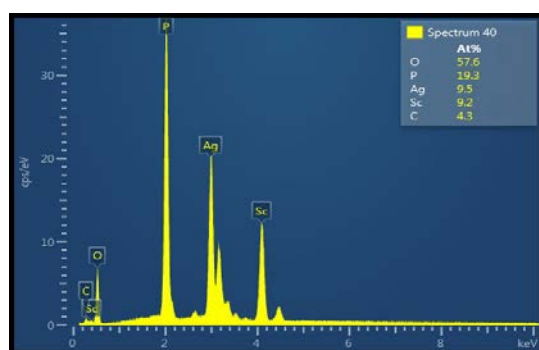


Figure 3. The EDAX spectrum of $\text{AgScHP}_3\text{O}_{10}$.

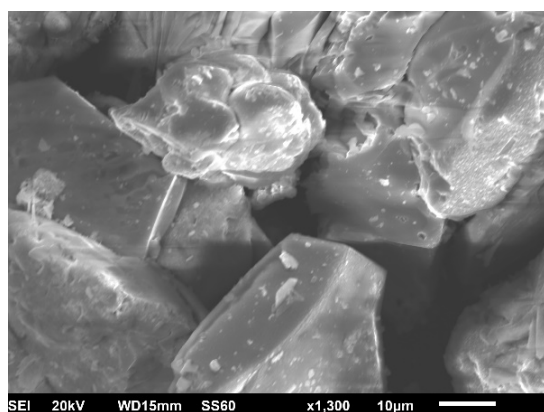


Figure 4. Electron (SEI) image of $\text{AgSc}(\text{H}_2\text{P}_2\text{O}_7)_2$ (enlargement 1300).

Table 6. Data for spectrum 22, Site 1, molar ratio $\text{Ag}/\text{Ga} = 5.0$, synthesis at 335°C , approximate formula $[\text{AgGa}(\text{PO}_3)_4]$

Atom	Atomic %
O	73.41
P	14.71
Ga	4.07
Ag	7.81

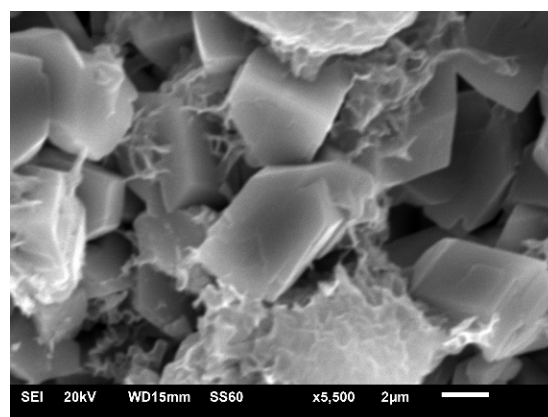


Figure 5. Electron (SEI) image of $\text{AgSc}(\text{H}_2\text{P}_2\text{O}_7)_2$ (enlargement 5500).

Figure 6 shows the SEM picture of silver scandium cyclotetraphosphate ($\text{AgScP}_4\text{O}_{12}$) synthesized at the temperature of 335°C at the molar ratio $\text{Ag}/\text{Sc} = 5.0$.

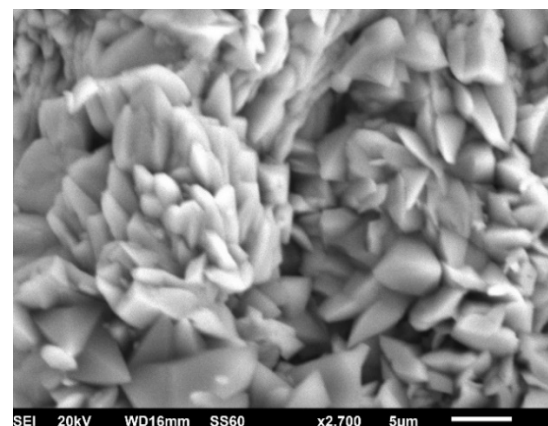


Figure 6. Electron (SEI) image of $\text{AgScP}_4\text{O}_{12}$ (enlargement 2700).

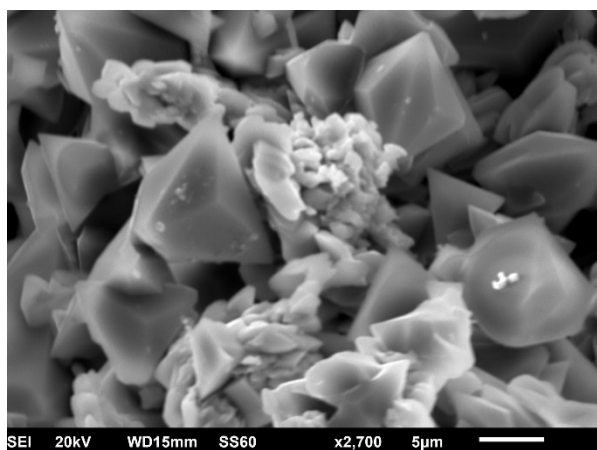


Figure 7. Electron (SEI) image of cyclododecaphosphate $\text{Ag}_3\text{Ga}_3\text{P}_{12}\text{O}_{36}$ (as primary phase) with the small impurity phase of the cyclotetraphosphate $\text{AgGaP}_4\text{O}_{12}$ (enlargement 2700).

A detailed XRD analysis of the components formed in the system $\text{Ag}_2\text{O}-\text{Ga}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ allows us to conclude that the product obtained at temperature 335 °C and for $n=\text{Ag}/\text{Ga}=7.5$ consists of two phases such as silver gallium cyclododecaphosphate $\text{Ag}_3\text{Ga}_3\text{P}_{12}\text{O}_{36}$ (as primary phase) and the and silver gallium cyclotetraphosphate $\text{AgGaP}_4\text{O}_{12}$. Figure 7 shows the electron image for silver gallium cyclododecaphosphate with a small mix phase – the minor quantity of silver gallium tetraphosphate. The synthesis conditions were as follows: $\text{Ag}/\text{Ga}=7.5$ and temperature 335°C.

Conclusions

The formation of $\text{Me}^I\text{Me}^{III}(\text{H}_2\text{P}_2\text{O}_7)_2$, $\text{Me}^I\text{Me}^{III}(\text{H}_2\text{P}_2\text{O}_7)_2\text{H}_2\text{O}$, $\text{Me}^I\text{Me}^{III}\text{HP}_3\text{O}_{10}$, and $\text{Me}^I\text{Me}^{III}\text{P}_4\text{O}_{12}$ type crystalline double phosphates could be detected in the systems $\text{Me}^I_2\text{O}-\text{Me}^{III}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ ($\text{Me}^I=\text{Ag}$, $\text{Me}^{III}=\text{Ga}$, In and Sc) in the temperature range of 130–600 °C at $\text{Ag}/\text{Me}^{III}=1.5-10.0$ and $\text{P}/\text{Me}^{III}=15.5$ molar ratio. The obtained crystalline phases were identified with the chemical analysis, XRD and EDAX. The silver scandium, silver gallium and silver indium cyclotetraphosphates are isomorphic with each other and with sodium gallium cyclododecaphosphate.

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References

- Avaliani, M. A., Tananaev, I. V., Gvelesiani, M. K., Synthesis and investigation of double condensed phosphates of scandium and alkali metals, in: *Phosphorus, Sulfur, Silicon & Related Elements*, **1990**, publish. Taylor&Francis online **2009**, *51*(1-4), 453-453. <https://doi.org/10.1080/10426509008040977>.
- Averbuch-Pouchot, M.-Th., Durif, A. Topics in Phosphate Chemistry, Singapore, *World Sci.*, ISBN-13:978-9810226343, **1996**, 174-209.
- Avaliani, M. A., Synthesis and characterization of gallium and Indium condensed phosphates (*PhD Thesis*), Moscow, N. Kurnakoff Inst. General & Inorg. Chem., **1982**, 5-184.
- Avaliani, M. A., Tananaev, I. V., Gvelesiani, M. K., Gaprindashvili, V. N., Synthesis and investigation of double condensed phosphates of scandium and alkali metals. *ChemInform Abstract*, **1991**, <https://doi.org/10.1002/chin.199102035>
- Grunze, I., Palkina, K. K., Chudinova, N.N., Avaliani, M. A., Guzeeva, L.S., Structure and thermal transitions of double Cs–Ca phosphates. *Inorg. Mater.*, **1987**, *23*(4), 539-544, OSTI ID: 5847982
- Avaliani, M. A., Double sodium–scandium phosphates. *Inorg. Mater.*, **1990**, *26*(12), *INIS* *23*(15), 2647-2648. https://inis.iaea.org/search/search.aspx?orig_q=RN:23046460
- Avaliani, M., Concerning applications of condensed phosphates of tri- and polyvalent metals. *Proc. Georgian Acad. Sci. (Chem. Ser.)*, **2004**, *30*(1/2), 36-39.
- Avaliani, M., Shapakidze, E., Barnovi, N., Gvelesiani, M., Dzanashvili, D., About new inorganic polymers-double condensed phosphates of silver and trivalent metals. *J. Chem. & Chem. Eng.*, **2017**, *11*, 60-64. DOI: [10.17265/1934-7375/2017.02.004](https://doi.org/10.17265/1934-7375/2017.02.004)
- Murashova, E. V., Chudinova, N. N., Condensed cesium-indium phosphates, *Inorg. Mater.*, **2001**, *37*(12), 1298-1301. DOI: [10.1023/A:1012938428228](https://doi.org/10.1023/A:1012938428228)
- Avaliani, M., Investigation and thermal behaviour of double condensed compounds of gallium, scandium and silver, *Nano Studies*, **2018**, *17*(18), 21-24. DOI: [10.13140/RG.2.2.13040.76807](https://doi.org/10.13140/RG.2.2.13040.76807)
- Avaliani, M.A., Kveselava, V.M., Esakia N.A. Determination of trivalent metals: gallium, indium and scandium by oxyquinoline, *Georgia Chem. J.*, **2018**, *1*(18), 17-26. DOI: [10.13140/RG.2.2.13028.42880](https://doi.org/10.13140/RG.2.2.13028.42880)
- Bandurkin, G. A., Chudinova, N.N., Palkina, K.K., Balagina, G. M., Komova, M. G., Cationic (metallic) “memory” in double condensed phosphates: Metals Ln-oxides Ln_2O_3 -phosphates ($\text{MLn}(\text{PO}_3)_4$ and $\text{MLnP}_4\text{O}_{12}$). *Russ. J. Inorg. Chem.*, **2008**, *53*(7), 1077-1089. DOI: [10.1134/S0036023608070176](https://doi.org/10.1134/S0036023608070176)
- Durif, A. Crystal Chemistry of Condensed Phosphates. Cyclooctaphosphates. Cyclododecaphosphates, *Plenum Press*, 2nd edition, **2013**, 318-441.
- Oudahmane, A., D. Avignant, D., Zambon, D., Dipotassium dialuminium cyclo-octa-phosphate.. *Acta Crystallogr. E*, **2010**, *66*(7), 49-50. DOI: [10.1107/S1600536810020751](https://doi.org/10.1107/S1600536810020751).
- Bandurkin, G. A., Chudinova, N. N., Lysanova, G. V. Krut'ko, V. A., Palkina, K. K., Komova, M. G. Heavy lanthanide phosphates: nanostructuring during their solid-phase synthesis. *Russ. J. Inorg. Chem.*, **2006**, *51*(9), 1473-1482. DOI: [10.1134/S0036023606090117](https://doi.org/10.1134/S0036023606090117)
- Chudinova, N.N., Murashova, E. V. Yluikhin. A. B., Double cyclohexaphosphates of cesium and divalent metals. *Inorg. Mater.*, **2003**, *39*(12), 1298-1302. DOI: [10.1023/B:INMA.0000008917.97768.ab](https://doi.org/10.1023/B:INMA.0000008917.97768.ab)
- Avaliani, M., Barnovi, N., Esakia, N., Sh. Makhatadze. Apropos of inorganic polymers. Condensed phosphates as inorganic polymers and various domains of their applications, *Proc. Georgian Acad. Sci. (Chem. Ser.)*, **2015**, *41*(3), 227-231. DOI: [10.13140/RG.2.2.31613.82408/1](https://doi.org/10.13140/RG.2.2.31613.82408/1)
- Avaliani, M., Dzanashvili, D., Shapakidze, E., Esakia, N., New inorganic polymers: condensed phosphates and diverse spheres of their applications, in: *book of abst. 26th Ann. World Forum Adv. Mater. "Polychar"*, **2018**, *1*, 101-101. DOI: [10.13140/RG.2.2.16320.58885](https://doi.org/10.13140/RG.2.2.16320.58885)

- ¹⁹Avaliani, M., Gvelesiani, M., Areas of crystallization of condensed scandium and cesium phosphates and regularities of their formation. *Proc. Georg. Acad. Sci. (Chem.Ser.)*, **2006**, 32(1-2), 52-58.
- ²⁰Grunze, I., Palkina, K. K., Chudinova, N. N., Guzeeva, L. S., Avaliani, M.A., Maksimova, S. I. Structure and thermal rearrangements of binary cesium-gallium phosphates. *ChemInform Abs.*, **1987**, 18(28), 610-615. <https://doi.org/10.1002/chin.198728010>
- ²¹Marsh, T. P., Studies into the ion exchange and intercalation properties of $\text{AlH}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ (Ph.D. Thesis), *ed.of Univ. Birmingham*, **2011**, 6-77. <http://etheses.bham.ac.uk/id/eprint/1599>
- ²²Hore, K., The investigation of condensed phosphates of alkaline earth metals for use as biomaterials, *etheses.bham.ac.uk, Univ. Birmingham*, **2011**, 13-32. <https://pdfs.semanticscholar.org/d3a4/327779e92b8eb3b58759a6a5fcdf787d24d9.pdf>
- ²³Avaliani, M. A., Chagelishvili, V.A., Gvelesiani, M. K., Barnovi N. V., Kveselava, V.M. Esakia, N. A., Shapakidze, E. V., Areas of crystallization of condensed scandium and silver phosphates and regularities of their formation, *5th Intern. Conf. Nanotechnologies, «NANO-2018»*, **2018**, 1, 15-16. DOI: [10.13140/RG.2.2.27447.78241](https://doi.org/10.13140/RG.2.2.27447.78241)
- ²⁴Avaliani, M., Shapakidze, E., Areas of crystallization of double condensed phosphates of Ag and trivalent metals, *5th Int. Conf. Org. & Inorg. Chem. "Strategic Approach & Future Generation Advancements in Organic & Inorganic Chemistry"*, Paris, *J Chemical Sci*, **2018**, 9, 63-63. DOI: [10.4172/2150-3494-C4-027](https://doi.org/10.4172/2150-3494-C4-027)
- ²⁵Avaliani, M., Barnovi, N., Gvelesiani, M. Esakia, N., Double condensed phosphate's chemistry of mono- and trivalent metals. *Georgia Chem. J.*, **2017**, 17(1), 6-11.
- ²⁶Vassel, N. P., Vassel, S. S., Pavlova, I. V., Kakliugin, A. V., Thermal study of systems involving the metaphosphates of trivalent metals and silver. *Proc. Inst. Higher Edu. (Phys.)*, **2011**, 1(2), 121-124.
- ²⁷Avaliani M., Shapakidze E., Barnovi N., Dzanashvili D., Todradze G., Kveselava V., Gongadze N. Regio-controlled synthesis of double condensed oligo-, poly- and cyclo- phosphates, their characterization and possibilities of applications, due to their solid-state properties. *Nano Studies*, **2019**, 19 (in press).
- ²⁸Harris D.Ch. Quantitative Chemical Analysis. Gravimetric analysis, precipitation titrations and combustion analysis. (*8th edition*), by W. H. Freeman & Co, **2010**, 673-691.
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