INVESTIGATIONS OF PHASE EQUILIBRIUM IN THE SYSTEMS
 $M_2O_3 - P_2O_5 - H_2O$, $M = Al, Ga, In$ AND $Tl(III)$
BY THIN LAYER METHOD: COMPOUNDS FORMATION AND
PROPERTIES OF NOVEL PHOSPHATES

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Abstract Phase equilibrium in the systems $M_2O_3-P_2O_5-H_2O$, $M = Al, Ga, In$ and $Tl(III)$ (molar ratio $P_2O_5:M_2O_3 = (3\div 10):1$) have been studied within the temperature range of 25-300°C by thin layer method. The crystallization fields diagrams of stable phases were plotted. Preparation conditions of a number of novel phosphates, $MH_9(PO_4)_4$ ($M = Al, Ga, In$), $M(H_2PO_4)_3$ ($M = Ga, In, Tl$), $M_3H_{15}(PO_4)_8 \cdot 5H_2O$ ($M = Ga, In$), $MH_3(PO_4)_2 \cdot 4H_2O$ ($M = Ga, Tl$), $TlH_3(PO_4)_2 \cdot nH_2O$ ($n = 0, 1, 2, 4$), $Ga(H_2PO_4)(H_2P_2O_7)$, $TlHP_2O_7$, $In_3H_7(P_2O_7)_4$, $InH_2P_3O_{10}$, $In_2H_2P_2O_7(P_4O_{12})$, and $Tl(PO_3)_3$ were elaborated. Main regularities in formation of compounds in the studied systems are discussed.

INTRODUCTION

This report is part of extensive investigation of reactions in the systems $M_2O_3-P_2O_5-H_2O$, where M are practically all trivalent metals: Al, Ga, In and Tl (p -elements of the 3rd group of the Periodic system); Sc, Ti, V, Cr, Mn and Fe (d -elements of the 3rd period); $Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb$ and Lu (rare earth metals); Au, Bi etc. This investigations include a study of phase equilibrium in the systems $M_2O_3-P_2O_5-H_2O$ and design of the crystallization fields diagrams within the large temperature range covering crystallization fields of phosphates with the most various composition and anion structure: from hydrate of hydroorthophosphates to poly- and ultraphosphates. The studied realized in identical conditions will furnish to establish

dependencies of the crystallization rate on radius and electron structure of trivalent cation. Investigations include a detailed comparative study of properties of novel phosphates too.

EXPERIMENTAL PROCEDURE

Reactions in the systems M_2O_3 - P_2O_5 - H_2O , where $M = Al, Ga, In$ and $Tl(III)$ (molar ratio $P_2O_5:M_2O_3 = (3\div 10):1$) have been studied within the temperature range of 25-300°C by thin layer method (TLM) specially developed previously to investigate a phase equilibrium in the viscous hardly crystallizing systems containing a volatile component.¹ The reagents, Al_2O_3 , Ga_2O_3 , In_2O_3 , $Ga(NO_3)_3 \cdot 8H_2O$, $In(NO_3)_3 \cdot 4,5H_2O$, $Tl(OH)_3$, H_3PO_4 ($d = 1,7$) (all Reakhim products) were used. According to TLM, initial homogeneous mixtures of a given composition with molar ratio of $P_2O_5/M_2O_3 = 3, 4, 5, 6, 7, 8, 9$, and 10 have been holded in several millimetres thickness layer of solution or solution-melt at given temperature and relative humidity (RH). The RH was maintained nearly 50-60%. At 25°C different values of RH were given in hermetic boxes with the help of hydrostatics. An occurrence of equilibrium has been checked by X-ray powder diffraction (XRD) and visually using optical microscopy. Then temperature or relative humidity has been changed, and investigations have been followed. All novel crystalline compounds were separated from the unreacted mixture by washing with water or water/acetone mixture and dried at room temperature. Novel phosphates were identified by chemical analysis, XRD, quantitative thin layer chromatography, and IR spectroscopy.

RESULT AND DISCUSSION

In accordance with the TLM data, the M_2O_3 - P_2O_5 - H_2O systems were found to contain the following stable phases within corresponding temperature ranges (see Figure), the formation of stable compounds being not depend practically on the P_2O_5/M_2O_3 proportion in the studied molar ratio $P_2O_5:M_2O_3 = (3\div 10):1$. The formation of stable phases is determined only by temperature and RH values.

T, °C	M ₂ O ₃ -P ₂ O ₅ -H ₂ O			
	Al	Ga ^{2,3}	In ^{4,5}	Tl ⁶
300	Al ₄ (P ₄ O ₁₂) ₃	M(PO ₃) ₃ - C		
275				
250				
225	AlH ₂ P ₃ O ₁₀ -II			
200	AlH ₂ P ₃ O ₁₀ -I	GaH ₂ P ₃ O ₁₀ -II	In ₂ H ₂ P ₂ O ₇ (P ₄ O ₁₂)	
175		GaH ₂ P ₃ O ₁₀ -I		
150			In ₃ H ₇ (P ₂ O ₇) ₄	
125				
100	Al(H ₂ PO ₄) ₃ -C	GaH ₄ (PO ₄)(P ₂ O ₇)	In(H ₂ PO ₄) ₃ -B	Tl(H ₂ PO ₄) ₃
75		Ga(H ₂ PO ₄) ₃ -C		
50				
25		M ₃ H ₁₅ (PO ₄) ₈ 5H ₂ O		

FIGURE. Comparative diagram of crystallization fields of stable phases in the systems M₂O₃-P₂O₅-H₂O, where M = Al, Ga, In and Tl(III) (molar ratio P₂O₅:M₂O₃ = (3÷10):1).

Besides, the following compounds have been identified as unstable phases:

- in the system Al₂O₃-P₂O₅-H₂O - AlH₉(PO₄)₄ (form I at 100°C and form II at 25°C);
- in the system Ga₂O₃-P₂O₅-H₂O - GaH₉(PO₄)₄ (form II at 25°C); GaH₃(PO₄)₂ nH₂O (n = 2, 5; 4) (at 25°C);
- in the system In₂O₃-P₂O₅-H₂O - InH₉(PO₄)₄ (form II at 25°C); InH₃(PO₄)₂ 4H₂O (at 25°C) and InH₂P₃O₁₀-form II (at 175°C)
- in the system Tl₂O₃-P₂O₅-H₂O - TlH₃(PO₄)₂ (at 75°C); TlH₃(PO₄)₂ nH₂O (n = 2, 4) (at 25°C).

Figure shows the main regularities in compounds formation in the studied systems. All diagrams have the same character, but an increasing of three valence metal radius from Al to Tl leads to decreasing of crystallization temperature range of oligophosphates (from 125 to 75° accordingly) and a sequential change from triphosphates to pyrophosphates crystallization under this conditions.

In addition, the relative humidity influence on phases formation in the systems at 25°C were studied. An increasing of RH value from 0 to 100% was found to result in the

step-by-step crystallization of the following compounds: $\text{MH}_9(\text{PO}_4)_4$ - $\text{M}(\text{H}_2\text{PO}_4)_3$ - $\text{M}_3\text{H}_{15}(\text{PO}_4)_8 \cdot 5\text{H}_2\text{O}$ - $\text{MH}_3(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 1 \div 4$) - $\text{MPO}_4 \cdot 2\text{H}_2\text{O}$.

SUMMARY

In this work we studied phase equilibrium in the systems $\text{M}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$, $\text{M} = \text{Al, Ga, In and Tl(III)}$ (molar ratio $\text{P}_2\text{O}_5\text{:M}_2\text{O}_3 = (3 \div 10)\text{:1}$) within the temperature range of 25-300°C by thin layer method. As results the crystallization fields diagrams of stable phases were plotted, and preparation conditions of a number of novel phosphates, two anion-mixed acidic orthopyro- and pyrocyclotetraphosphate among them, were elaborated. An increasing of trivalent metal radius from Al to Tl was found to result in a decrease of crystallization temperature range oligophosphates (from 125 to 75° accordingly) and a sequential change from triphosphates to pyrophosphates crystallization under this conditions.

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