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Influence of fluorides on phase relations in the molten systems M^I_2O-P_2O_5 Mn_2O_3/$M^{II}O$, M^I – Li, Na, K; M^{II} – Ni, Co

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Addition of alkaline fluorides to molten phosphates with a composition M^I_2O-P_2O_5-Mn_2O_3 and M^I_2O-P_2O_5-$M^{II}O$ (M^I – Li, Na, K) gradually changes the solubility of polyvalent metals oxides and shifts the crystallization areas in the corresponding melts. The results obtained are based on solubility curves found for Mn_2O_3, CoO and NiO in the fluxes of M^I_2O-P_2O_5 -MF and M^I_2O-P_2O_5 -MF (where M^I – Li, Na, K) and X-Ray diffraction, IR spectroscopy and thermal analysis. The presence of 10 and 20 % mass of fluorides provides molten polyphosphates depolymerization and yields pyro- $Li_2MnP_2O_7$, $K_2CoP_2O_7$, $Na_2CoP_2O_7$ and orthophosphates $Na_2Mn_3(P_2O_7)_2$, $NaMnPO_4$, $NaNiPO_4$ single crystals growth.

Introduction

Complex phosphates composed of transition and alkaline metals exhibit outstanding behavior among other solids leading to a wide area of applications in modern techniques. These compounds are known to show advanced properties such as highly-efficient luminescence, high chemical and thermal stability, high conductivity and unique catalytic behavior [1-3]. Due to a high thermal stability of the majority of phosphates, the flux- growth method provides a successful avenue to discover and grow single crystalline materials so that structure –physical property relationships may be determined. Optimization of crystal growth media offers not only compositional, size and shape control in tailored crystal growth, but also shows potential for introducing different doping agents that are problematic for other conventional methods. The growth of high quality pure and doped single crystals is necessary to elucidate the intrinsic electronic and thermodynamic properties and has played a significant role in advancing basic and applied materials research.

The interaction of oxides in a series of phosphate systems of M^I_2O-P_2O_5-Me_xO_y (where M^I – Li, Na, K; Me – Fe, Co, Ni, Mn, Cr, Al, Ti, Sc) in a wide range of molar ratios and temperatures has been already systematically investigated and a series of phosphates has been discovered: $M^IM^{II}(PO_3)_3$, $M^IM^{II}PO_4$, $M^I_2M^{II}P_2O_7$, $M^I_2M^{II}(PO_3)_4$,$M^I_2M^{II}(PO_3)_4$, $M^IM^{II}_4(PO_4)_3$, $M^I_3M^{III}(PO_4)_2$, $M^I_3M^{III}_2$ $(PO_4)_3$, $M^IM^{III}P_2O_7$ and $M^IM^{III}(PO_3)_4$ [4-9]. Importantly, the conditions of these compounds preparation require continuous annealing under high temperature due to a low solubility of polyvalent metals' oxides within phosphate media [1].

To overcome this difficulty one can propose application of an additional solvent, that can lower homogenization temperature and improve solubility of oxides discussed. In this article the use of alkaline metal fluorides has been proposed as sufficient high temperature flux for a binary phosphates growth. The influence of fluoride component has been studied by estimation of solubility cures for the $M^{II}O$ and Mn_2O_3 oxides in the binary melts and determination of the crystallization fields for the phosphates containing alkaline and transition metals.

The main attention has been paid to giving an overview of relationship between composition and nature of flux systems used and composition of compounds formed and structure–property correlations of a selected group of complex phosphates to demonstrate the potential for growth and discovery of materials for different applications using high temperature crystal growth technique.

Experimental part

Systematic investigation has been performed for the phosphate molten salts containing fluorides as inert media. The initial reagents, $M^I_2CO_3$, $M^IH_2PO_4$, $M^I_2HPO_4$, M^IF (M^I – Li, Na, K), $(NH_4)_2HPO_4$, NiO, CoO, Mn_2O_3 (analitycally pure, 99.99 %) have been mixed in ratios corresponding to molar ratios M^I/P =0.5-2.0. To prepare fluxes with molar ratios M^I/P <1,0 diammonium phosphate $(NH_4)_2HPO_4$ or $NH_4H_2PO_4$ was used as a phosphate source. To prepare fluxes with molar ratios M^I/P>1,0 alkaline metal phosphates $M^IH_2PO_4$, $M^I_2HPO_4$ have been used.

In each experiment raw materials corresponding to different salts ratio without polyvalent metal oxide have been transferred to a platinum crucible and placed in a resistive heating vertical single zone furnace attached with eurotherm controller to enable the crystal growth process with the following scheme: (1) the temperature is increased from room temperature to 970 °C at a rate of 200 °C/h to melt the mixture of the precursors. (2) At this stage calculated amount of

Mn_2O_3 or $M^{II}O$ is added to the molten salts under stirring. (3) Then the mixture is kept at 970 °C for a period of 6 h in order to homogenize the mixture (4). Then it is cooled from 970 °C to 800 °C at the rate of 50 °C/h to initiate nucleation and facilitate the crystal growth. (5) The solid solution is cooled down to room temperature and then crystals are washed from the solidified melt with hot distilled water.

Solubility curves have been studied by saturation method. Homogenized fluxes of M_2O-P_2O_5-M^IF systems have been gradually saturated with manganese (III) oxide or NiO/CoO at the definite temperature during 7-10 hours till the crystal-liquid equilibrium is reached. The samples of the liquid phase have been investigated to find out the polyvalent metal content by titrimetric analysis. The remaining flux has been cooled as described above. Products have been examined by IR spectroscopy and powder X-ray diffraction (XRD). The experiment has carried out using a DRON-2 diffractometer (Cu Kα radiation, = 1.54184 A°; step size 0.02; range 2Θ=10–60).(Tables 1-3 Supplementary data) The thermal analysis has been carried out on MOM Q-1500D (Paulik-Paulik-Erdey) derivatograph at a heating rate of 5 °C·s^{-1} (in a platinum crucible, accuracy of ± 5 ºC, thermocouple Pt/Pt-Rh). The IR spectra have been recorded in KBr discs using a Nicolet Nexus FTIR spectrometer in a range of 400 – 4000 cm^{-1}

Results and discussion

On the first stage of the investigation the solubility curves have been investigated under different fluoride content (**Figure 1**). In case of Mn_2O_3 the solubility lowers smoothly with the M^I/P increase. The increase in fluoride content from 10 to 20% mass gives small impact on the position the solubility curves.

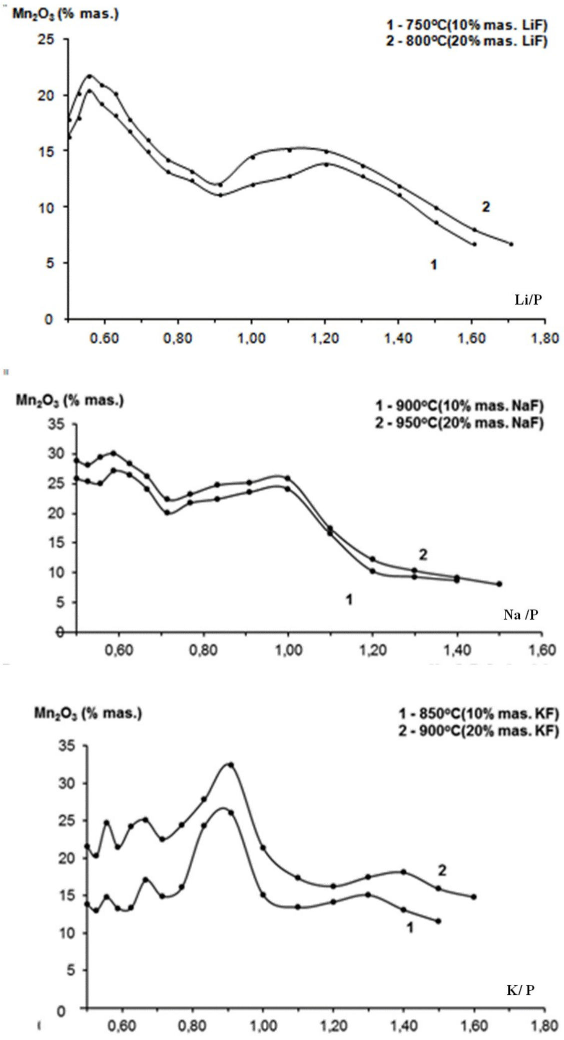

Figure 1. Solubility curves for systems M^I_2O-P_2O_5 -MF - Mn_2O_3, where M^I – Li, Na, K

In case of NiO and CoO the complex nature of solubility curves mostly depends on the alkaline metal nature and the viscosity of the melts prepared. While in case of NiO systems the content of fluoride does not influence the behavior significantly (**Figure 2**), the CoO solubility decreases dramatically for lithium and potassium-containing systems.

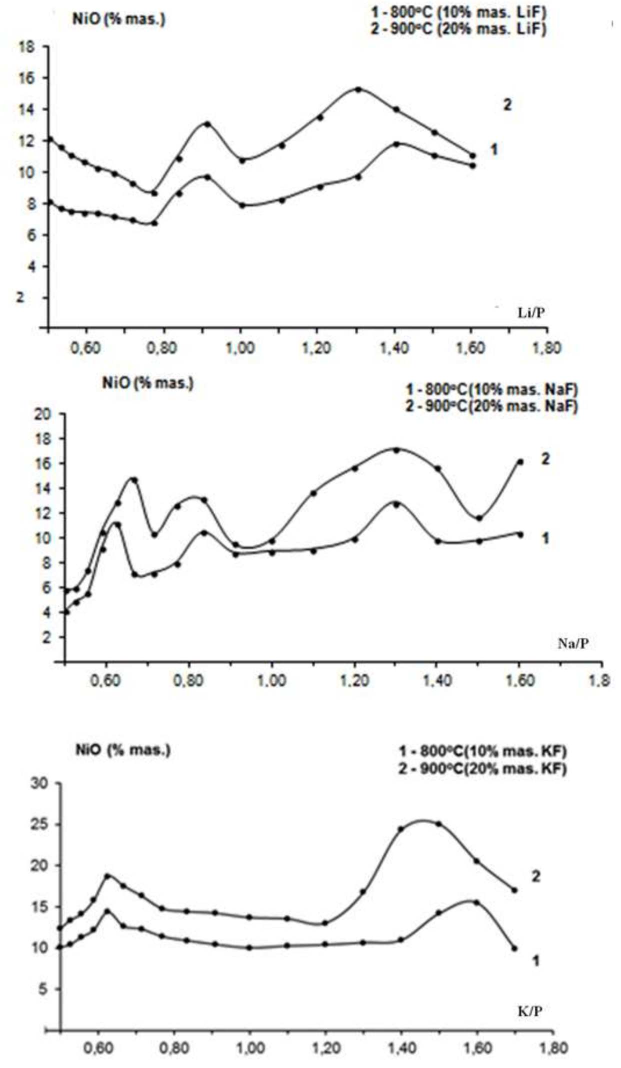

Figure 2. Solubility curves for systems M^I_2O-P_2O_5 -MF -NiO, where M^I – Li, Na, K

The interactions of manganese (III), cobalt (II) and nickel (II) oxides with phosphate media without fluorides have been reported previously [1,10-11] and solubility curves have been constructed. The crystallization fields of different compounds have been taken for comparison to show the influence of fluoride component.

Generally, addition of a fluoride component leads to crystallization field shift of binary phosphates areas toward lower M^I/P ratio (**Table 1**). Moreover, novel phases $Li_2MnP_2O_7$ (monoclinic system, C2c, a = 9.8941(6)Å, b = 9.8111(1)Å, c = 11.1597(8)Å, β= 102.482°) and $NaMnPO_4$ (orthorhombic system, Pnma, a = 5.172(1)Å, b = 6.98(1)Å, c = 9.214(1) Å) appear in case of the highest fluoride content. Unfortunately, the majority of the phosphates that can be grown from sodium-containing molten salt are shifted due to a stabilization of Mn^{3+} by fluoride component.

Table 1. The crystallization conditions and phases identified for M_2O-P_2O_5-Mn_2O_3-MF molten system

Compound	M^I/P mole ratios and M^IF content,% mass		
	0	10	20
Li_2O-P_2O_5-Mn_2O_3-LiF			
$Li_2Mn(PO_3)_4$	0.5-0.76	-	-
$Li_2MnP_2O_7$	-	-	0.5-0.62
β-$Mn_2P_2O_7$	0.76-1.3	0.5-1.0	0.62-1.0
$Mn_2P_2O_7$	1.3-1.8	1.0-1.7	1.0-1.7
Na_2O-P_2O_5-Mn_2O_3-NaF			
$Na_2MnP_2O_7$	0.91-1,2	0.76-1.4	0.5-0.76
$Mn_2P_2O_7$	0.66-0.71	-	-
$Mn_4(P_2O_7)_3$	0.71-0.76	-	-
$NaMn_6P_7O_{24}$	0.66	0.5-0.52	-
$NaMn(PO_3)_3$	0.5-0.83	-	-
$Na_2Mn_3(P_2O_7)_2$	-	0.52-0.76	-
$NaMnPO_4$	-	-	0.76-1.5
K_2O-P_2O_5-Mn_2O_3-KF			
α-$Mn_2P_2O_7$	0.5-0.56	-	-
$KMn_6P_7O_{24}$	0.56-0.66	0.5-0.58	0.5-0.56
$K_4Mn_4(P_2O_7)_3$	1.0-1.4	-	-
α-$K_2MnP_2O_7$	1.4-1.7	0.58-0.71	0.56-0.66
$K_2MnP_2O_7$	1.7-1.8	0.71-1,0	0.66-1.0
$KMnPO_4$	-	1.0-1.5	1.0-1.6

The solubility of nickel oxide in binary phosphate-fluoride melt containing 20%mass of fluoride at 900° C increases from lithium- (15.31% mass) to potassium containing system (**Figure 2**).

Table 2. The crystallization conditions and phases identified for M_2O-P_2O_5-NiO-MF molten system

Compound	M^I/P mole ratios and M^IF content, %mass		
	0	10	20
Li_2O-P_2O_5-NiO-LiF			
$Ni(PO_3)_2$	0.5-0.83	0.5-0.83	0.5-0.56
$Li_2Ni_4(PO_4)_2P_2O_7$	0.83-1.0	0.83-1.6	0.56-1.1
$Li_2Ni_3(P_2O_7)_2$	1.0-1.5	-	-
$LiNiPO_4$	1.5-1.8	-	1.1-1.7
Na_2O-P_2O_5-NiO-NaF			
$NaNi(PO_3)_3$	0.5-0.66	0.5-0.52	-
$Ni(PO_3)_2$	0.56-0.66	0.52-0.58	-
$Ni_2P_2O_7$	0.56-0.83	-	-
$Na_3Ni_2(PO_3)_3P_2O_7$	0.66-0.71	-	-
$Na_2NiP_2O_7$	1.0-1.2	0.58-1.0	0.5-1.0
$Na_4Ni_3(PO_4)_2P_2O_7$	1.2-1.6	1.0-1.5	-
$NaNiPO_4$	-	1.5-1.6	1.0-1.6
K_2O-P_2O_5-NiO-KF			
$Ni(PO_3)_2$	0.5-0.66	-	-
$K_6Ni_3(PO_3)_4(P_2O_7)_2$	0.66-0.71	0.5-1.0	0.5-1.0
$K_2NiP_2O_7$	0.66-0.71	-	-
$KNi(PO_3)_3$	0.66-0.71	-	-
$KNiPO_4$	0.83-1.0	-	-
$K_2Ni_4(PO_4)_2P_2O_7$	1.1-1.4	1.0-1.7	1.0-1.7

It should be pointed out that quite opposite trend has been found for fluoride-free phosphate fluxes of M_2O-P_2O_5-NiO systems – the solubility of NiO increases from potassium (16.2% mass)– to lithium phosphate system (19.3% mass) [6]. The crystallization regions changes significantly (**Table 2**). As one can admit, addition of 10% mass of fluoride to a phosphate melt containing NiO leads to a better structural diversity of the compounds prepared. Application of high fluoride content narrows the area of the compound prepared. Importantly, formation of $Ni(PO_3)_2$ (monoclinic system, C2c, a = 7.220 (6)Å, b = 7.220 (1)Å, c = 9.785 (8)Å, β= 109.561°), $Li_2Ni_4(PO_4)_2(P_2O_7)$ (monoclinic system, $P2_1/c$, a = 6.3589(4) Å, b = 10.7795(6) Å, c = 10.3836(6) Å, β = 90.019(1)°), and $LiNiPO_4$ (orthorhombic system, Pnma, a = 10.015(1)Å, b = 5.848(1)Å, c = 4.617(1) Å) phosphates is typical for lithium-containing fluoride-phosphate system, instead the compound $Li_2Ni_3(P_2O_7)_2$ (monoclinic system, P21/c, a = 7.285 (4) Å, b = 7.875 (6) Å, c= 9.442 (6) Å, β = 110.128 (1))°is crystallized only in case of presence of lithium fluoride.

In Na_2O-P_2O_5-NiO-NaF system (containing 10% mass of NaF) at 800° C a set of known phosphates is identified: $NaNi(PO_3)_3$ (orthorhombic system, Pcca, a = 13.781(2) Å, b = 10.584(2) Å, c = 9.873(1) Å), $Ni(PO_3)_2$ (monoclinic system, C2c, a = 7.240 (6)Å, b = 7.212 (1)Å, c = 9.685 (8)Å, β= 109.561°), $Na_2NiP_2O_7$, $Na_4Ni_3(PO_4)_2P_2O_7$ and $NaNiPO_4$. Higher fluoride content (20% mass) in the fluxes results in a formation of only two phosphates in a wide range of molar ratios Na/P – $Na_2NiP_2O_7$ (from 0.5 to 1.0) та $NaNiPO_4$ (from 1.0 to 1.6).

Only two complex phosphates are identified in potassium-containing systems: $K_6Ni_3(PO_3)_4(P_2O_7)_2$ and $K_2Ni_4(PO_4)_2(P_2O_7)$ at

800° C and 900° C in the fluxes of K_2O-P_2O_5-NiO-KF.

In comparison to NiO, cobalt-containg system shows the same trend described above. The solubility of cobalt oxide in the alkali metal fluorides and phosphate fluorides fluxes increases from LiF (27.6% mass) to KF (32.3% mass) system. Only three areas of phosphates crystallization $Li_4Co_4(PO_3)_8P_2O_7$, $LiCoPO_4$ and $LiCo_2P_3O_{10}$ are found for Li_2O-P_2O_5-CoO-LiF molten system (**Table 3**).

The phosphate $LiCo_2P_3O_{10}$ has not been found for Li_2O-P_2O_5-CoO system. Importantly, the areas of other known phosphates $LiCoPO_4$ (from 0.5 to 1.1) and $Li_4Co_4(PO_3)_8P_2O_7$ (from 1.1 to 1.7) have become wider.

Table 3. The crystallization conditions and phases identified for M_2O-P_2O_5-CoO-MF molten system

Compound	M^I/P mole ratios and M^IF content,%mass		
	0	10	20
Li_2O-P_2O_5-CoO-LiF			
$Co(PO_3)_2$	0.5-0.71	-	-
$Li_2Co_4(PO_4)_2P_2O_7$	0.71-0.83	-	-
$Li_2CoP_2O_7$	0.83-1.0	-	-
$Li_4Co_3(PO_4)_2P_2O_7$	1.0-1.15	-	-
$Li_4Co_4(PO_3)_8P_2O_7$	1.15-1.25	1.0-1.7	1.1-1.7
$LiCoPO_4$	1.35-1.45	0.56-1.0	0.5-1.1
$Li_4Co_4(P_2O_7)_3$	1.45-1.55	-	-
Na_2O-P_2O_5-CoO-NaF			
$NaCo(PO_3)_3$	0.5-0.66	-	-
$NaCo_3(PO_4)P_2O_7$	0.66-0.76	-	-
$Co_2P_2O_7$	0.76-0.96	-	-
$Na_6Co(P_2O_7)_2$	0.96-1.1	0.83-1.6	0.91-1.6
$Na_4Co_3(PO_4)_2P_2O_7$	1.1-1.2	0.66-0.83	-
$NaCoPO_4$	1.2-1.5	-	-
$Na_2CoP_2O_7$	-	0.5-0.66	0.50-0.91
K_2O-P_2O_5-CoO-KF			
$KCoPO_4$	0.91-1.5	0.91-1.7	0.91-1.7
$K_2Co_3(P_2O_7)_2$	0.5-0.62	-	-
$K_2CoP_2O_7$	-	0.5-0.91	0.5-0.91

Fluxes containing 10% mass of sodium fluoride are characterized by three double phosphates areas, namely, $Na_4Co_3(PO_4)_2P_2O_7$, $Na_2CoP_2O_7$ and $Na_6Co(P_2O_7)_2$. An increase in sodium fluoride content leads to the formation of only two latter compounds and widening of the corresponding areas to Na/P=1.0-1.2 molar ratios. Unlike Na_2O-P_2O_5-CoO system, double pyrophosphate $Na_2CoP_2O_7$ in the fluxes of Na_2O-P_2O_5-CoO-NaF melts is crystallized. In case of K_2O-P_2O_5-CoO-KF system, like in fluoride-free system, only two compounds are formed: double orthophosphate $KCoPO_4$ and phosphate $K_2CoP_2O_7$.

Thus, one can conclude, that 10% mass of fluoride component shows better result in optimization of growth conditions of a series of complex phosphates containing nickel, cobalt and manganese. One of the most known features of fluoride component is a depolymerization function of P-O-P condensed chains in the melt [11]. Taking into consideration that M^I/P ratio shifts the areas of crystallization of pyrophosphates and orthophosphates in the same direction, an admixture of fluoride can been seen as an additional factor of tailoring the composition for grown crystalline materials.

Conclusions

Application of an inert fluoride flux for direct phosphates crystal growth influences the solubility of oxides used for interaction with a phosphate media and shifts the crystallization regions of the phosphates prepared. Importantly, the depolymerization role of a fluoride in the melts is more likely to be a key factor in new phosphates crystal growth. Thus, pyrophopshates $Li_2MnP_2O_7$, $K_2CoP_2O_7$, $Na_2CoP_2O_7$ and orthophosphates $Na_2Mn_3(P_2O_7)_2$, $NaMnPO_4$, $NaNiPO_4$ have been shown to crystallize only in a presence of a fluoride component. Thus, an approach proposed may be used for other functional materials crystal growth and optimization of synthesis conditions of know compounds.

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