SYNTHESIS AND PHASE FORMATION IN THE FLUX SYSTEM $K_2O–P_2O_5–Nb_2O_5–MoO_3$

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Oxide functional materials based on niobium possess distinct physical properties providing extensive application field. Complex phosphates take a special place among the oxide matrices owing to thermal stability and chemical resistance in combination with special features of crystal structure.

The flux growth and preliminary investigations of crystalline compounds obtained in pseudo-four-component system $K_2O–Nb_2O_5–P_2O_5–MoO_3$ are reported here. Synthesis of single crystals was carried out in a medium of melted $K_2Mo_2O_7$. FTIR and X-ray powder diffraction methods were applied for identification of compounds obtained. The concentration ranges of crystallization fields of three types of compounds were established: potassium polyniobates (A), molybdatoniobates (B) and phosphoniobates (C). The analysis of FTIR spectra proved the presence in C-type compounds specific absorption bands of phosphate tetrahedra PO_4 [ν_{as}(P–O); 980–1185 cm^{-1}] and biphosphate groups P_2O_7 [ν_{as}(P–O–P); 930–980 cm^{-1}]. By comparison of spectra of A- and B-type compounds it was found that A-type has a set of absorption bands related to NbO_6 octahedra at 622–886 cm^{-1}, while B-type could be easily distinguished by additional bands at 840–900 cm^{-1}. The latter fact indicates that Mo^{6+} is being in highly distorted six-fold oxygen environment. Variation of P_2O_5 maintenance at arbitrary selected section leads to increase of homogenization temperature from 700 to 1000 °C for $aK_2O–bNb_2O_5–cP_2O_5$ system (a = 3.18; b = 6–12; c = 1). In particular, potassium polyniobates (A) generated typically at lower maintenance of P_2O_5 component at the temperatures below 950 °C. The area (A) on the diagram $aK_2O–bNb_2O_5–cP_2O_5$ (a = 3,25–10,92; b = 0,67–11; c = 1) includes crystallization fields of two types of phases: blue needle-shaped crystals of composition KNb_3O_8 (sp. gr. *Amam*; a = 8.903(3); b = 21.16(4); c = 3.799(2) Å; V = 715.68(5) $Å^3$; Z = 4) and colorless plate-like crystals of $K_6Nb_{10+x}O_{30}$ (x = 0.5-0.8) type (sp. gr., *P*4/*mbm*; a = 12.582-12.590.; c = 3.992-4.008 Å; V = 631.96(8) $Å^3$; Z = 1). Otherwise, cooling of flux $aK_2O–bNb_2O_5–cP_2O_5$ (a = 1,56 –2.82; b = 1.41–1,50; c = 1) to 880 °C is resulted in crystallization of potassium molybdatoniobates (B) with common formula $K_{1-x}(Nb_{1-x}Mo_x)O_3$ (x = 0.3-0.5). C-type compounds are obtained in the temperature ranges 800-500 °C [$aK_2O–bNb_2O_5–cP_2O_5$ (a = 1.13–2.7; b = 0.5–4; c = 1)]. X-ray powder diffraction patterns of C-type crystalline samples are collected at first except the complex phosphates $K_{5+3x}Nb_{8-x}P_5O_{34}$ (ICDD #00–048–0097).