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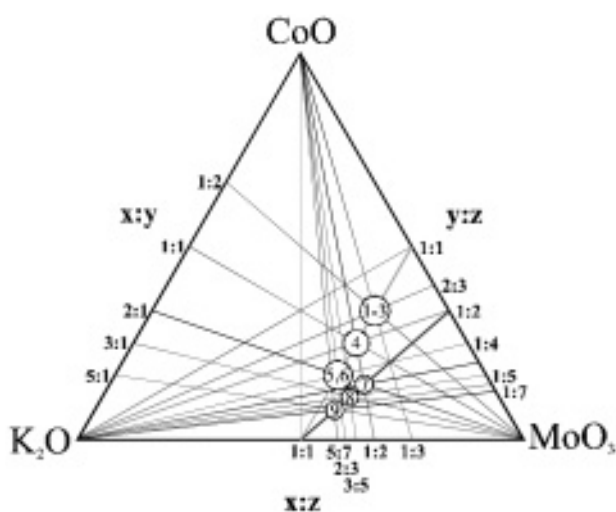
## Structure systematics in K-Co-Mo-O compounds

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The standard modifications of the phases in the K-Co-Mo-O-system belong either to the structure family  $K_{2n}CoMo_{2+n}O_{7+4n}$  [1-3] or to the orthooxomolybdates  $K_xCo_y(MoO_4)_z$  [4,5]. All completely characterised compounds of the K-Co-Mo-O-system exhibit oxidation states  $Mo^{6+}$  and  $Co^{2+}$ , respectively. All phases merge in one phase diagram presented here.



Scheme of crystalline K-Co-Mo-O phases: (1)  $\alpha$ - $K_2Co_2(MoO_4)_3$ , (2)  $\beta$ - $K_2Co_2(MoO_4)_3$ , (3)  $\alpha$ - $K_2Co_2(MoO_4)_3$ -II, (4)  $K_2Co(MoO_4)_2$ , (5)  $\alpha$ - $K_4Co(MoO_4)_3$ , (6)  $\beta$ - $K_4Co(MoO_4)_3$ , (7)  $K_4CoMo_4O_{15}$ , (8)  $K_6CoMo_5O_{19}$  and (9)  $K_{10}CoMo_7O_{27}$ .

Apparently, all known phases belong to one of two stability lines: Orthooxomolybdates are situated on the green line and the  $K_{2n}CoMo_{2+n}O_{7+4n}$  compounds are located at the blue line. The established compounds at normal conditions feature either isolated  $[MoO_4]$ -tetrahedra (green) or face sharing  $[CoO_6]$ - $[MoO_6]$ -octahedra (blue). In addition to the ambient condition phases, both a high-temperature and a high-pressure phase were found for  $K_2Co_2Mo_3O_{12}$  and  $K_4CoMo_3O_{12}$ .

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## Crystal Chemical Features of $Na_2FeTi(PO_4)_3$ and $Rb_2FeTi(PO_4)_3$ Orthophosphates with NZP Structure Type

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Crystal structures of synthetic phosphates obtained by sol-gel technique  $Na_2FeTi(PO_4)_3$  and  $Rb_2FeTi(PO_4)_3$  which belong to the NZP (sodium zirconium phosphate) structure type [1], have been refined by Rietveld method using X-ray powder diffraction data. NZP structure type is of interest because: 1) the framework formed by  $[PO_4]$ -tetrahedra and octahedra of Zr, Ti, Fe and other atoms is stable; 2) cavities of the framework can accommodate both small and large atoms, in oxidation state from +1 to +5. So, the compounds with NZP structure type can be considered as: 1) promising matrices for immobilization of actinides and heavy metal atoms; 2) high-strength ceramic materials which can be used in the industry.

The results of investigation of synthetic phosphates  $Na_2FeTi(PO_4)_3$  and  $Rb_2FeTi(PO_4)_3$  by microprobe and Rietveld analysis are the following: the replacement in the mixed tetrahedral-octahedral framework of two Na atoms ( $r_a = 1.86 \text{ \AA}$ ) by two Rb atoms ( $r_a = 2.48 \text{ \AA}$ ) with larger atomic radii leads to changing of symmetry from rhombohedral in the structure of  $Na_2FeTi(PO_4)_3$  (sp. gr.  $R-3c$ ,  $a = 8.6015(1)$ ,  $c = 21.718(1) \text{ \AA}$ ,  $R_{wp} = 4.42\%$ ), up to cubic in the structure of  $Rb_2FeTi(PO_4)_3$  (sp. gr.  $P2_13$ ,  $a = 9.8892(2) \text{ \AA}$ ,  $R_{wp} = 4.33\%$ ). This fact shows the increase of durability and stability of an investigated framework. The results obtained evidently demonstrate dependence of crystal structure features of investigated compounds from their chemical composition. This work was partly supported by The Grant of the President of the Russian Federation, Support of Young Russian Scientists and Leading Scientific Schools of the Russian Federation, no. MK-935.2005.5.

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