SYNTHESIS AND MICROSTRUCTURE OF CUBIC G0-$Rb_2KMoO_3F_3$ OXYFLUORIDE

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Rubidium potassium oxyfluoromolybdate, $Rb_2KMoO_3F_3$, is a member of wide oxyfluoride family $A_2BMO_3F_3$ (A, B = Na, K, Rb, Cs, Tl, NH_4, Ag; M = Mo, W) with elpasolite-related crystal structure. Complete O/F disorder in the anion positions, however, is found for high temperature cubic G0-phase with space group *Fm*-3*m*. Commonly, the polarity of $MoO_{6-x}F_x$ octahedron is strongly dependent on O/F ratio with maximum at O/F = 3. Respectively, to have reproducible results on phase composition and physical properties of an oxyfluoride the technology should be stabilized with respect to fluoride component loss during synthesis. It should be also accounted that the appearance of Mo^{4+} and Mo^{5+} ions is possible due to incomplete oxidation of molybdenum atoms in nonstoichiometric oxyfluoromolybdates possessing noticeable electrical conductivity. Thus, the present study is aimed at the design of technology for the stable synthesis of G0-$Rb_2KMoO_3F_3$ compound and the observation of structural and morphological properties of the final product.

The $Rb_2KMoO_3F_3$ compound was formed by solid state synthesis in accordance with the earlier proposed reaction: $2RbF + KF + MoO_3 = Rb_2KMoO_3F_3$. High purity initial reagents $KF{\times}2H_2O$, Rb_2CO_3, MoO_3, NH_4F and aqueous hydrofluoric acid (HF) (48% HF by weight) were used. To avoid the drastic capture of air agents into KF and RbF reagents, all the reactions and heat treatments were produced under dried nitrogen atmosphere at increased pressure. KF was synthesized by vaporization of a mixture of $KF{\times}2H_2O$ and hydrofluoric acid. The starting mixture of KF, RbF and MoO_3 was prepared in stoichiometric composition ratio related to $Rb_2KMoO_3F_3$ nominal. The mixture was grinded, placed into the open platinum crucible and heated to T = 1073 K at the rate of 100 K/h. Then, the melt was being cooled to room temperature together with furnace for t = 24 h. The final product of the reaction in the melt was a dense uniform milk color disk-like agglomerate of ~35 mm in diameter and ~10 mm in thickness.

The micromorphology of the product was evaluated with scanning electron microscopy (SEM) using LEO 1430 device. Chemical composition and molybdenum valence state were defined by X-ray photoelectron spectroscopy (XPS) method. The chemical composition of $Rb_2KMoO_3F_3$ sample was estimated with XPS using the Rb 3d, K $3p_{3/2}$, Mo $3d_{5/2}$, O 1s and F 1s lines and tabulated atomic sensitivity factors as Rb:K:Mo:O:F = 0.21:0.10:0.09:0.35:0.25. The powder X-ray diffraction pattern for Rietveld analysis was collected at room temperature (298 K) with a Bruker D8 ADVANCE diffractometer. The elpasolite-related crystal structure of G0-$Rb_2KMoO_3F_3$ has been refined by Rietveld method at T = 298 K (space group *Fm*-3*m*, a = 8.92446(8) Å, V = 710.76(1) $Å^3$; R_B = 3.55 %).