



## Exploration on anion ordering, optical properties and electronic structure in $K_3WO_3F_3$ elpasolite

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### ABSTRACT

Room-temperature modification of potassium oxyfluorotungstate,  $G2-K_3WO_3F_3$ , has been prepared by low-temperature chemical route and single crystal growth. Wide optical transparency range of 0.3–9.4  $\mu\text{m}$  and forbidden band gap  $E_g=4.32$  eV have been obtained for  $G2-K_3WO_3F_3$  crystal. Meanwhile, its electronic structure has been calculated with the first-principles calculations. The good agreement between the theoretical and experimental results have been achieved. Furthermore,  $G2-K_3WO_3F_3$  is predicted to possess the relatively large nonlinear optical coefficients.

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### 1. Introduction

Complex metal oxyfluorides are attractive compounds for creation new noncentrosymmetric crystals because the strong distortion of metal-(O,F) polyhedra in crystal lattice is achieved due to different ionicity of metal-O and metal-F bonds. This strategy is particularly successful in design of new oxyfluoroborates containing boron-(O,F) polyhedra and possessing interesting nonlinear optical properties and wide transparency range [1–4]. Effects of mixed anion sublattice, however, are considered for a long time for a suite of transition metals compounds with  $[MO_{6-x}F_x]$  ( $M=W, Mo, Nb, Ti$ ) groups [5–11]. From geometrical point of view, the strongest distortion of separated  $[MO_{6-x}F_x]$  octahedron is achieved for  $x=3$  and such polar structural group seems to be optimal for generation of low-symmetry complex compounds [6]. These distorted octahedrons can be stacked without the center of inversion in the crystal lattice if long range ordering condition is fulfilled. Indeed, several noncentrosymmetric inorganic crystals containing ordered  $[MO_3F_3]$  ( $M=Mo, W$ ) groups were found at enough low temperatures [6,10,12–16].

Oxyfluorides  $A_2BMO_3F_3$  ( $A, B=Na, K, Rb, Cs, Tl, NH_4$ ;  $M=Mo, W$ ) show similar structural, ferroelectric and ferroelastic properties

within the certain temperature intervals [10,13,14,17,18]. Cubic paraelectric phase  $G0$  with elpasolite-type parent structure in space group  $Fm-3m$  has been found for  $A_2BMO_3F_3$  compounds at high temperature range  $T > T_1$  [8,9,16,18–21]. Complete disorder in anion positions is a principal characteristic of this state. At low temperatures  $T \leq T_1$  partial anion ordering results in subsequent phase transitions with formation of low-symmetry phases  $G_i$ . For many  $A_2BMO_3F_3$  compounds the structural transitions are accompanied by noticeable dielectric and calorific effects [10,13,14,17,18,20,22–24]. Piezoelectric  $G_i$ -phases were found for several cation compositions but detailed information on physical properties of the compounds is practically absent in literature for lack of oxyfluoride single crystals with size and quality needed for the measurements. To our best knowledge, only the few-hundred- $\mu\text{m}$ -size  $Rb_2KMoO_3F_3$ ,  $K_3MoO_3F_3$ ,  $(Ag_3MoO_3F_3)(Ag_3MoO_4)Cl$ ,  $Ag_3MoO_3F_3$  and  $Ag_3VO_2F_4$  crystals were grown up to now because of the great technological difficulty to grow oxyfluoride crystals with reasonable size [19,25,26].

For the representative compound  $K_3WO_3F_3$  from  $A_2BMO_3F_3$  family, the transitions of ferroelectric  $G0 \leftrightarrow G1$  and ferroelastic  $G1 \leftrightarrow G2$  character were defined to be at  $T_1=452$  K and  $T_2=414$  K, respectively [10,14,17,27]. The entropy variation under the transition was found to be  $\Delta S_1=R\ln(1.68)$  and  $\Delta S_2=R\ln(1.42)$  [10,14]. Crystal structures of  $G1-K_3WO_3F_3$  and  $G2-K_3WO_3F_3$  modifications were refined by powder methods in space groups  $I4mm$  and  $Cm$ , respectively, with evident indication of  $O^{2-}$  and  $F^-$  ion ordering at anion positions [15,16]. Vibrational spectra and

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electronic structure of G2- $K_3WO_3F_3$  were examined with Raman, IR and X-ray photoelectron spectroscopy (XPS) for powder samples [27,28]. Noticeable variation of W–O mean bond ionicity in G2- $K_3WO_3F_3$ , as it seems due to presence of W–F bonds, was found by XPS in reference to that in pure tungstates [29]. However, other properties of  $K_3WO_3F_3$  remain to be unclear. Present study is aimed to grow the crystals of low-temperature ferroelectric G2- $K_3WO_3F_3$  polymorph. Optical properties and electronic structure are then evaluated comparatively by experimental and theoretical methods.

## 2. Experimental

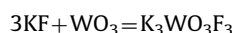
### 2.1. Chemical synthesis and crystal growth

Powder sample of  $K_3WO_3F_3$  was fabricated by low-temperature chemical synthesis from water-based solutions. As starting reagents the KF (99.9%) and  $K_2WO_4$  (99.5%) were used. At a first step a solution of potassium fluoride in hydrofluoric acid was prepared. After this, a solution of potassium tungstate in distilled water was carried out. Then, these two solutions were mixed with precautions because the reaction is active and with heating. As a result of reaction, white precipitate was separated out of mother solution. After drying a white-colored powder product was formed.

Water-free KF and  $WO_3$  were used as starting materials to produce  $K_3WO_3F_3$  single crystals. Water-free KF was obtained by evaporating  $KF \times 2H_2O$  with adding of concentrated etching acid.  $NH_4F$  was added to dry the remainder and resulting substance was heated to 300 °C in a teflon crucible to remove the remained water and alkali according the following reaction:



The obtained substance was heated to 500 °C in closed Pt crucible in presence of teflon which was used as a fluorine agent. Then substance was grinded in a mortar, mixed with teflon boring and placed into a Pt crucible with a cover. The crucible was heated to 900 °C, the temperature above KF melting temperature, in a flow of dry nitrogen. Before using,  $WO_3$  was heated to 700 °C in a Pt crucible. The synthesis of  $K_3WO_3F_3$  compound was carried out from a charge of stoichiometric composition:



The mixture was grinded in a mortar and placed into a Pt ampule. The ampule was then located on a chamotte support inside a growth furnace and covered with a Pt cover, under which dry nitrogen was delivered during the whole growth experiment. The furnace was heated to 980 °C at a 30 °C/h rate. Then furnace was kept at this temperature during 6 h and afterwards temperature was lowered during 2 day at a rate of 1 °C/h. The obtained crystal was cooled at a rate of 30 °C/h. In a result the cm-size  $K_3WO_3F_3$  single crystals were formed by this technique as shown in Fig. 1. The crystals are transparent and enough large for optical measurements. It should be pointed that presently crystal growth technology is well developed only for nonlinear optical oxyfluoroborates. As to other oxyfluorides, typically powder samples formed by chemical synthesis are used for physical properties observation [8,10,13–18,20,23]. For several oxyfluorides tiny single crystals were fabricated with dimensions enough for single crystal structure determination [12,19,21,26]. To our best knowledge, up to now preparation of optical quality mm-size crystals was achieved only for  $K_3MoO_3F_3$ ,  $(NH_4)_2WO_2F_4$  and  $(NH_4)_2NbOF_5$  compounds [25,30,31]. The technology developed in present



Fig. 1. Photo of  $K_3WO_3F_3$  single crystal on the background of Times Roman font 12.

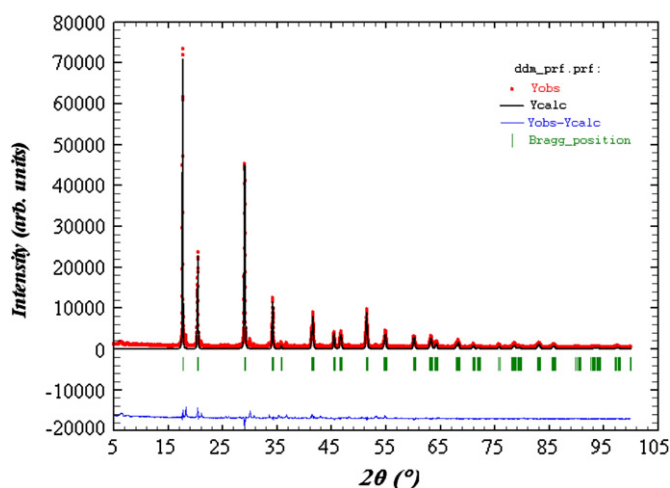


Fig. 2. XRD analysis of  $K_3WO_3F_3$  crystal at room temperature.  $Cm$  space group.

study for creation of large  $K_3WO_3F_3$  is universal and can be applied for other oxyfluorides.

Phase composition of grown  $K_3WO_3F_3$  crystal at room temperature was evaluated with XRD analysis. The results of the XRD analysis are shown in Fig. 2. Presence of pure monoclinic G2- $K_2WO_3F_3$ , space group  $Cm$ , modification was found with structural parameters  $a=8.7459(2)$  Å,  $b=8.6930(4)$  Å,  $c=6.1650(3)$  Å,  $\beta=135.178(2)^\circ$ .

### 2.2. Structure determination

Structure determination of G0, G1 and G2 polymorph modifications of  $K_3WO_3F_3$  has been produced with Rietveld analysis for powder sample prepared by chemical synthesis. The powder X-ray diffraction patterns were collected at 298, 433 and 513 K with a Bruker D8 ADVANCE diffractometer in the Bragg-Brentano geometry and linear Vantec detector [16]. Operating parameters were:  $CuK_\alpha$  radiation, tube voltage 40 kV, tube current 40 mA, step size  $0.016^\circ$ , counting time 1 s per step. The data were collected over the range 5–110°. Peak positions were determined with the program EVA, available in the PC software package DIFFRAC-PLUS supplied from Bruker. X-ray patterns of the title compound were indexed using the program McMaille [33]. The details of the analysis (e.g., R-factors) for the diffraction data sets

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