



Structural and electronic parameters of ferroelectric $K_3WO_3F_3$

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ABSTRACT

The low-temperature ferroelectric G2 polymorph of $K_3WO_3F_3$ oxyfluoride is formed by chemical synthesis. The electronic parameters of G2- $K_3WO_3F_3$ have been measured by X-ray photoelectron spectroscopy under excitation with Al $K\alpha$ radiation (1486.6 eV). Detailed spectra have been recorded for all element core levels and Auger lines. The chemical bonding effects in the WO_3F_3 and WO_6 octahedrons are considered by using the binding energy difference $\Delta BE(O-W) = BE(O\ 1s) - BE(W\ 4f_{7/2})$.

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1. Introduction

Potassium oxofluorotungstate, $K_3WO_3F_3$, is a representative member of the wide crystal family $A_2BMO_3F_3$ ($A, B = K, Rb, Cs$; $M = Mo, W$), possessing a set of phase transitions from paraelectric G0 to ferroelectric G1 and G2 states on cooling [1–4]. More recently, the set of A and B cations possible in this oxyfluoride family was completed by Na, Tl, NH_4 and Ag [5–10]. From a geometrical point of view, very strong distortion of the MO_3F_3 polyhedron is evident due to the different ionicity of the M–O and M–F bonds, and this factor is promising for high ferroelectricity if the polyhedra are packed in an orderly fashion [11]. Complete disorder of the anion positions, however, is found for many $A_2BMO_3F_3$ compounds in the high-temperature G0 state [3–9,12]. Partial ordering of the anion positions on decreasing the temperature, however, results in the appearance of an acentric crystal structure and spontaneous polarization in the G1 and G2 states [3–6,13].

$K_3WO_3F_3$ is among several compounds from the $A_2BMO_3F_3$ crystal family whose ferroelectric transition temperature is noticeably above room temperature. In the high-temperature state at $T > T_2 = 452$ K, G0- $K_3WO_3F_3$ is characterized by a cubic perovskite-type structure with space group $Fm\bar{3}m$ [3,4,14]. Over the interval $T_2 > T > T_1 = 414$ K, G1- $K_3WO_3F_3$ has an acentric crystal structure and ferroelectric properties [3,4,14]. At room temperature ($T < T_1$), G2- $K_3WO_3F_3$ is a ferroelectric, space group

Cm , with partial ordering of the O/F positions [13]. As regards other physical and chemical properties of $A_2BMO_3F_3$ compounds, the information is very scarce. The present study is aimed at evaluating the electronic parameters of the low-temperature monoclinic modification G2- $K_3WO_3F_3$ with the help of X-ray photoelectron spectroscopy (XPS) and considering the bonding effects that appear due to presence of two different anions, O^{2+} and F^- , with comparable ionicity in the crystal lattice.

2. Experimental

Ferroelectric $K_3WO_3F_3$ was fabricated by low-temperature chemical synthesis. Initially a solution of KF in hydrofluoric acid was prepared. After this, a solution of potassium tungstate in distilled water was prepared. Then, these two solutions were mixed with precautions because the reaction is active and it produces heat. As a result of the reaction, a white precipitate was separated out of the mother solution. The micromorphology and chemical composition of the final product were evaluated by scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA), respectively, with the help of a LEO 1430 device. The phase composition of the final product was identified by X-ray diffraction (XRD) analysis using a D8-ADVANCE device with Cu $K\alpha$ radiation and θ – 2θ scanning. Only a few low-intensity peaks related to foreign phases were present in the XRD spectrum obtained from G2- $K_3WO_3F_3$ [13].

Observation of the electronic parameters of G2- $K_3WO_3F_3$ was undertaken by using a surface analysis center SSC (Riber) with the XPS method. Nonmonochromatic Al $K\alpha$ radiation (1486.6 eV)

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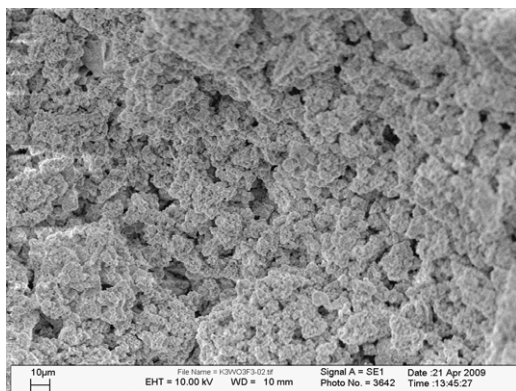


Fig. 1. SEM image of G2- $K_3WO_3F_3$ microparticles formed by chemical synthesis.

with a power source of 300 W was used for the excitation of photoemission. The energy resolution of the instrument was chosen to be 0.7 eV, so as to have sufficiently small broadening of the natural core level lines at a reasonable signal-to-noise ratio. Under these conditions the observed full width at half maximum (FWHM) of the Au $4f_{7/2}$ line was 1.31 eV. The binding energy (BE) scale was calibrated in reference to the Cu $3p_{3/2}$ (75.1 eV) and Cu $2p_{3/2}$ (932.7 eV) lines, ensuring an accuracy of 0.1 eV in any peak energy position determination. Photoelectron energy drift due to charging effects was taken into account in reference to the position of the C 1s (284.6 eV) line generated by adventitious carbon on the surface of the powder as inserted into the vacuum chamber.

3. Results and discussion

The morphology of the G2- $K_3WO_3F_3$ microparticles is shown in Fig. 1. There are no well-faceted grains because of the swift precipitation as a result of the chemical reaction. At the same time, the XRD spectrum confirms the high crystallinity of the final product [13]. In Fig. 2, the survey photoemission spectrum recorded is presented. Besides the constituent element core levels and Auger lines the low-intensity signals of C 1s and Na 1s levels were detected. It seems that the C 1s line is related to adventitious hydrocarbons captured by the particle surface from air, and the sodium admixture that appeared is due to traces in the original reagents. The valence band and W 4f doublet are shown in Fig. 3. An ionic gap over the BE range 10–12 eV is evident in the valence band of G2- $K_3WO_3F_3$. Mixed states are found at ~ 2.5 –10 eV and an intensive K 3p-related feature dominates at 16.6 eV. The O 2s-related and F 2s-related features are not well resolved, supposedly due to the mixed nature of the states. The BE value of the W $4f_{7/2}$ component (35.4 eV) is within the range of the W^{6+} state [15–21]. Also present on the low BE side of the W 4f doublet is a shoulder of low intensity. In Fig. 4, the C 1s line and K 2p doublet are shown. The C 1s line is wide and is evidently a multicomponent feature, and for BE scale calibration the value of 284.6 eV was assigned to maximum of the line. The components of the K 2p doublet are well resolved, and the BE value of the K $2p_{3/2}$ component (292.6 eV) is close to that found earlier for K^+ ions in several complex potassium-bearing crystals from the $KTiOPO_4$ and $KGd(WO_4)_2$ families [16,18,19,22–24]. The O 1s and F 1s core levels in G2- $K_3WO_3F_3$ are shown in Figs. 5 and 6 respectively.

The chemical composition of the sample determined by XPS is K:W:O:F = 0.33:0.08:0.27:0.32, which is close to the nominal formula $K_3WO_3F_3$. The atomic sensitivity factors reported in [15] were used in the calculations. The Auger parameters of constituent elements in G2- $K_3WO_3F_3$ were measured as $\alpha_K = 542.45$ eV, $\alpha_O = 1040.85$ eV and $\alpha_F = 1340.8$ eV. Table 1 contains the BE values obtained for the element core levels and Auger lines in G2- $K_3WO_3F_3$.

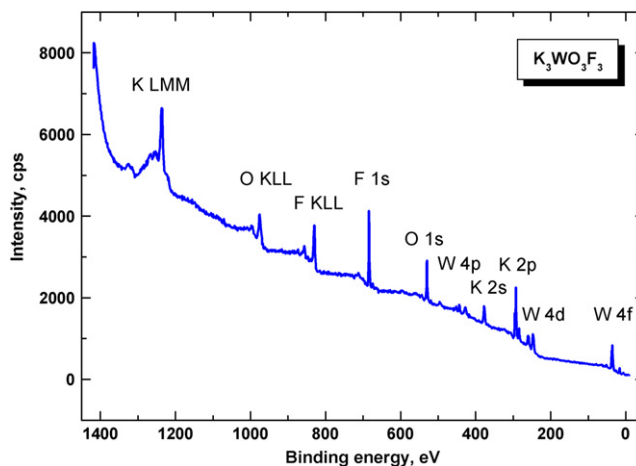


Fig. 2. Survey photoelectron spectrum recorded.

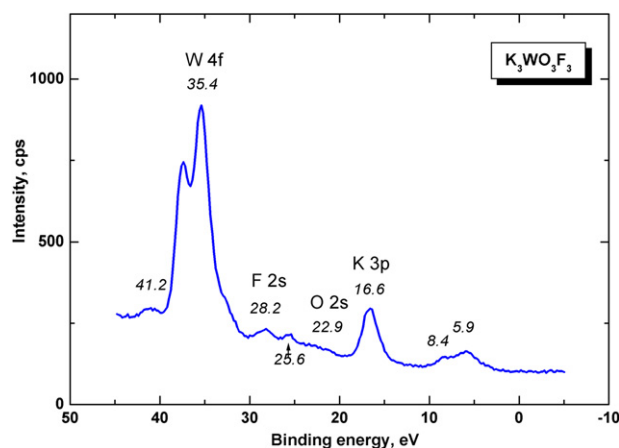


Fig. 3. Valence band and W 4f doublet.

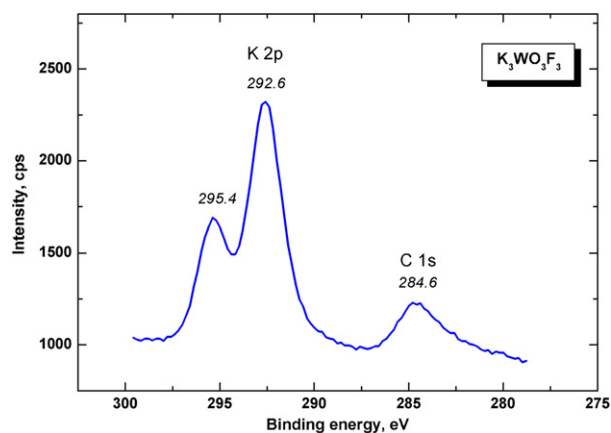


Fig. 4. K 2p-C 1s window.

To the best of our knowledge, this study is the first observation of the electronic structure of a complex compound containing the W^{6+} ion coordinated in parallel by O^{2-} and F^- ions. Earlier, in analyses of the electronic properties of different cations in complex oxides, use of the difference of BE values of the constituent element core levels was proposed as the best parameter for a description of the metal-oxygen (M-O) chemical bonding [16,18,19,23–30]. Numerous examples confirm the high robustness of such a difference BE parameter to drifting of the energy peak position induced by surface charging effects typical for dielectric materials [15]. Hence, the W-O chemical bonding in G2- $K_3WO_3F_3$

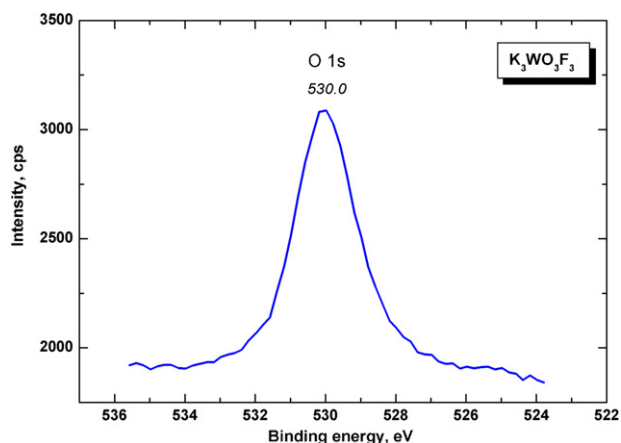


Fig. 5. O 1s core level.

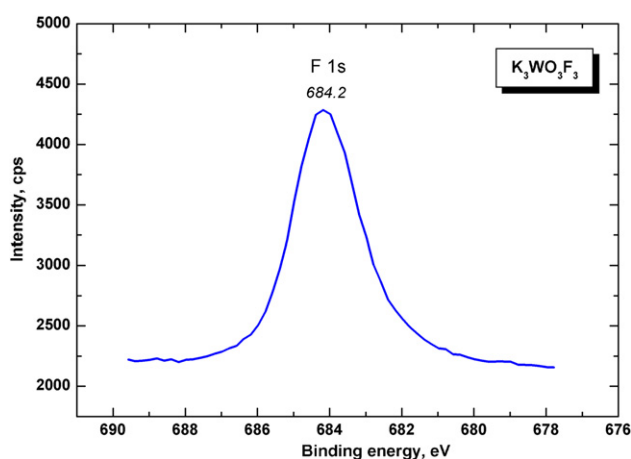


Fig. 6. F 1s core level.

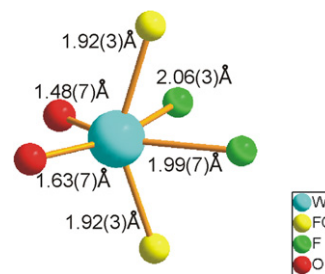
Table 1

Element core levels and Auger lines in G2-K₃WO₃F₃. The full width at half maximum (FWHM) of the element lines is presented in brackets.

Core level	Binding energy (eV)
VB	5.9, 8.4
K 3p	~16.6
O 2s	~22.9 (3.6)
F 2s	~28.2 (2.2)
W4f _{7/2}	35.4 (1.8)
W4f _{5/2}	37.6 (1.8)
W5p _{3/2}	41.2 (2.6)
W5p _{1/2}	~50.9 (4.6)
W4d _{5/2}	247.1 (4.7)
W4d _{3/2}	259.6 (4.9)
C 1s	Fixed at 284.6 (2.0)
K2p _{3/2}	292.6 (2.1)
K2p _{1/2}	295.4 (1.8)
K 2s	377.1 (3.8)
W4p _{3/2}	427.3 (~5.0)
W4p _{1/2}	492.5 (~5.0)
O 1s	630.0 (2.0)
F 1s	684.2 (2.0)
FKL ₂₃ L ₂₃	830.0
FKL ₁ L ₂₃	856.1
OKL ₂₃ L ₂₃	975.8
KL ₂₃ M ₂₃ M ₂₃	1235.7, 1237.9

was considered by using the energy difference $\Delta BE(O-W) = BE(O\ 1s) - BE(W\ 4f_{7/2})$ as a key parameter.

In the G2-K₃WO₃F₃ crystal lattice, all W atoms are in octahedral coordination, and each W atom is surrounded by two O atoms, two F atoms and two mixed (O, F) positions, as is illustrated in Fig. 7 [13]. The calculated mean chemical bond length for the

Fig. 7. WO₃F₃ octahedron in G2-K₃WO₃F₃.

tungsten–oxygen bond, $L(W-O) = 162$ pm, is evidently shorter than that of the tungsten–fluorine bond, $L(W-F) = 200$ pm, and the WO₃F₃ octahedron is strongly distorted. On the other hand, the values for $L(W-O)$ are 182.1 and 183.4 pm in KGd(WO₄)₂ and KY(WO₄)₂, respectively, with typical WO₆ octahedra [31, 32]. It seems that a compression of $L(W-O)$ in G2-K₃WO₃F₃ in comparison with KGd(WO₄)₂ and KY(WO₄)₂ takes place due to the presence of F atoms in the surroundings of the W. As regards the BE difference $\Delta BE(O-W) = BE(O\ 1s) - BE(W\ 4f_{7/2})$, the values are 494.6 eV for G2-K₃WO₃F₃ and 494.9 and 495.5 eV for KGd(WO₄)₂ and KY(WO₄)₂, respectively [16, 19]. So, shortening of $L(W-O)$ in G2-K₃WO₃F₃ is related to a lower $\Delta BE(O-W)$ value. Besides this, $\Delta BE(F-W) = BE(F\ 1s) - BE(W\ 4f_{7/2}) = 648.8$ eV, which relates to $L(W-F) = 200$ pm. This is the first determination of the $\Delta BE(F-W)$ parameter for W–F bonds.

4. Conclusions

The determination of structural and electronic parameters of G2-K₃WO₃F₃ gives an insight into specific features of W–O and W–F bonding in this crystal. The $\Delta BE(O-W)$ and $\Delta BE(F-W)$ electronic parameters were obtained by XPS and compared with available experimental data for two other complex tungstates with WO₆ octahedra. This comparison will be developed in future to investigate the variation of structural and electronic properties in WO_xF_{6-x} with variation of x [33, 34].

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References

- [1] G. Pausewang, W. Rüdorff, Z. Anorg. Allg. Chem. 364 (1969) 69–87.
- [2] A. Beuter, W. Sawodny, Z. Anorg. Allg. Chem. 381 (1971) 1–11.
- [3] G. Peraudeau, J. Ravez, P. Hagemuller, H. Arend, Solid State Commun. 27 (1978) 591–593.
- [4] J. Ravez, G. Peraudeau, H. Arend, S.C. Abrahams, P. Hagemuller, Ferroelectrics 26 (1980) 767–769.
- [5] Jean-Pierre Chaminade, Manuel Cervera-Marzal, Jean Ravez, Paul Hagemuller, Mater. Res. Bull. 21 (1986) 1209–1214.
- [6] F.J. Brink, L. Norén, R.L. Withers, J. Solid State Chem. 174 (2003) 44–51.
- [7] V.D. Fokina, I.N. Flerov, M.V. Gorev, M.S. Molokeev, A.D. Vasiliev, N.M. Laptash, Ferroelectrics 347 (2007) 60–64.
- [8] M.S. Molokeev, A.D. Vasiliev, A.G. Kocharova, Powder Diffr. 22 (3) (2007) 227–230.
- [9] I.N. Flerov, M.V. Gorev, V.D. Fokina, A.F. Bovina, M.S. Molokeev, E.I. Pogorel'tsev, N.M. Laptash, Phys. Solid State 49 (1) (2007) 141–147.
- [10] W. Tong, W.-S. Yoon, N.M. Hagh, G.G. Amatucci, Chem. Mater. 21 (2009) 2139–2148.
- [11] Paul A. Maggard, Tiffany S. Nault, Charlotte L. Stern, Kenneth R. Poeppelmeier, J. Solid State Chem. 175 (2003) 27–33.
- [12] S.C. Abrahams, J.L. Bernstein, Acta Crystallogr. B 37 (7) (1981) 1332–1336.
- [13] V.V. Atuchin, T.A. Gavrilova, V.G. Kesler, M.S. Molokeev, K.S. Aleksandrov, Chem. Phys. Lett. 493 (2010) 83–86.
- [14] I.N. Flerov, M.V. Gorev, V.D. Fokina, M.S. Molokeev, Ferroelectrics 346 (2007) 77–83.
- [15] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg (Eds.), Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp., Phys. Elect. Div., Minnesota, 1979.
- [16] V.V. Atuchin, V.G. Kesler, N.Yu. Maklakova, L.D. Pokrovsky, Solid State Commun. 133 (2005) 347–351.

- [17] O.Yu. Khyzhun, T. Strunskas, S. Cramm, Yu.M. Solonin, J. Alloys Compd. 389 (1–2) (2005) 14–20.
- [18] V.V. Atuchin, V.G. Kesler, N.Yu. Maklakova, L.D. Pokrovsky, D.V. Sheglov, Eur. Phys. J. B 51 (2006) 293–300.
- [19] V.V. Atuchin, L.D. Pokrovsky, O.Yu. Khyzhun, A.K. Sinelnichenko, C.V. Ramana, J. Appl. Phys. 104 (2008) 033518.
- [20] Yu-Xue Zhou, Hong-Bin Yao, Qiao Zhang, Jun-Yan Gong, Shu-Juan Liu, Shu-Hong Yu, Inorg. Chem. 48 (2009) 1082–1090.
- [21] S. Rajagopal, D. Nataraj, O.Yu. Khyzhun, Yahia Djaoued, J. Robichaud, D. Mangalaraj, J. Alloys Compd. 493 (2010) 340–345.
- [22] V.V. Atuchin, V.G. Kesler, N.Yu. Maklakova, L.D. Pokrovsky, V.N. Semenenko, Surf. Interface Anal. 34 (2002) 320–323.
- [23] V.V. Atuchin, O.A. Alekseeva, V.G. Kesler, L.D. Pokrovsky, N.I. Sorokina, V.I. Voronkova, J. Solid State Chem. 179 (8) (2006) 2349–2355.
- [24] C.V. Ramana, V.V. Atuchin, U. Becker, R.C. Ewing, L.I. Isaenko, O.Yu. Khyzhun, A.A. Merkulov, L.D. Pokrovsky, K. Sinelnichenko, S.A. Zhurkov, J. Phys. Chem. C 111 (6) (2007) 2702–2708.
- [25] V.V. Atuchin, L.D. Pokrovsky, V.G. Kesler, N.Yu. Maklakova, V.I. Voronkova, V.K. Yanovskii, Surf. Rev. Lett. 11 (2) (2004) 191–198.
- [26] V.V. Atuchin, I.E. Kalabin, V.G. Kesler, N.V. Pervukhina, J. Electron Spectrosc. Relat. Phenom. 142 (2005) 129–134.
- [27] V.V. Atuchin, V.G. Kesler, N.V. Pervukhina, Zhaoming Zhang, J. Electron Spectrosc. Relat. Phenom. 152 (1–2) (2006) 18–24.
- [28] C.V. Ramana, V.V. Atuchin, V.G. Kesler, V.A. Kochubey, L.D. Pokrovsky, V. Shutthanandan, U. Becker, R.C. Ewing, Appl. Surf. Sci. 253 (12) (2007) 5368–5374.
- [29] V.V. Atuchin, L.I. Isaenko, O.Yu. Khyzhun, L.D. Pokrovsky, A.K. Sinelnichenko, S.A. Zhurkov, Opt. Mater. 30 (7) (2008) 1149–1152.
- [30] V.V. Atuchin, V.G. Kesler, N.V. Pervukhina, Surf. Rev. Lett. 15 (4) (2008) 391–399.
- [31] M.C. Pujol, R. Solé, J. Massons, Jna. Gavaldà, X. Solans, C. Zaldo, F. Díaz, M. Aguiló, J. Appl. Crystallogr. 34 (2001) 1–6.
- [32] E. Gallucci, C. Goutaudier, G. Boulon, M.Th. Cohen-Adad, B.F. Mentzen, J. Cryst. Growth 209 (4) (2000) 895–905.
- [33] I.N. Flerov, M.V. Gorev, V.D. Fokina, A.F. Bovina, M.S. Molocheev, Y.V. Boiko, V.N. Voronov, A.G. Kocharova, Phys. Solid State 48 (1) (2006) 106–112.
- [34] I.N. Flerov, V.D. Fokina, M.V. Gorev, A.D. Vasiliev, A.F. Bovina, M.S. Molocheev, A.G. Kocharova, N.M. Laptash, Phys. Solid State 48 (4) (2006) 759–764.