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K_2SnOF_4 and $K_2WO_3F_2$ – different but similar

<https://doi.org/10.1515/znb-2020-0132>

Received July 31, 2020; accepted August 12, 2020; published online September 16, 2020

Abstract: K_2SnOF_4 and $K_2WO_3F_2$ were synthesized *via* a high-pressure/high-temperature route. Single-crystal analysis showed that both substances crystallize in the orthorhombic crystal system with space group $Pnma$ and are isostructural to each other. The main motifs of the structures are octahedral $[SnO_2F_4]^{4-}$ and $[WO_4F_2]^{4-}$ entities for K_2SnOF_4 and $K_2WO_3F_2$, respectively. Within the structures, these units are connected to quasi-isolated infinite chains. The substances were further characterized *via* powder X-ray diffraction, EDX and FT-IR spectroscopy. Doping of K_2SnOF_4 with Mn^{4+} yielded a red phosphor material which was analyzed by luminescence spectroscopy. The emission maximum is located at $\lambda_{max} = 631$ nm.

Keywords: crystal structure; potassium oxidofluoridostannate; potassium oxidofluoridotungstate.

1 Introduction

Oxidofluoridometallates offer a great structural diversity. Even though the most common building block is an octahedrally coordinated metal cation, other units, ranging from tetrahedrally to nonahedrally coordinated cations, can be observed. These units are either isolated, in single units or multinuclear motifs, or arranged in infinite chains, in layers, or even in 3-dimensional motifs [1]. In most of the examples reported to date, transition metals represent the central cations in oxidofluoridometallates. It is less common to observe main group elements within these compounds. For oxidofluoridotungstanates different octahedral units have been reported in the literature, *e.g.*,

the $[WO_4F_2]^{4-}$ unit observed within $Cs_2WO_3F_2$ or $Ba_2WO_3F_4$, the $[WO_3F_3]^{3-}$ unit observed within $K_3WO_3F_3$, the $[WO_2F_4]^{2-}$ unit observed within $K_3HF_2WO_2F_4$ and $A_2WO_2F_4$ ($A = NH_4$, Na, Rb, Cs), and the $[WOF_5]^-$ unit observed within K_3WOF_7 , $Ag(WOF_5)_2$, and $(XeF_2)(WOF_4)$ [2–13]. Some of these units, as well as other oxidofluoridometallates exhibiting similar units, recently gained some attention because of the possibility for partial substitution with Mn^{4+} which can produce materials exhibiting red luminescence upon blue light excitation [6–7, 14–18]. Regarding the $[WO_4F_2]^{4-}$ unit, which has been observed within the compound $Cs_2WO_3F_2$ by Mattes and Förster, and within $Ba_2WO_3F_4$ by Wingefeld and Hoppe, the octahedral units are connected to infinite chains [2, 8]. This connection is achieved through common oxygen atoms, which are located at *trans*-positions of the octahedra [2, 8]. The two fluorine atoms within this unit are located in the equatorial positions showing *cis*-configurations within both compounds [2, 8]. In contrast to this, oxidofluoridostannates are less common. Only the $[SnOF_5]^{3-}$ unit has been reported in the literature. It has been observed in the structure of $K_5Sn_2OF_{11}$ [19], where this unit forms quasi-isolated dinuclear motifs. [19]. Even though the $[SnO_2F_4]^{4-}$ unit was predicted for the compound K_2SnOF_4 by Kolditz and Preiss, this assumption has not yet been confirmed [20].

Therefore, we took the chance to analyze the crystal structures of K_2SnOF_4 and $K_2WO_3F_2$, exhibiting $[SnO_2F_4]^{4-}$ and $[WO_4F_2]^{4-}$ units, respectively, by means of single-crystal structure determination.

2 Experimental section

2.1 Synthesis

K_2SnOF_4 was synthesized from SnO_2 and KHF_2 *via* a high-pressure/high-temperature route. The educts were weighed in with an atomic ratio of 1 : 2.5 for Sn : K and firmly ground together. This step was carried out within a glove box (MBraun Inertgas-Systeme GmbH, Garching, Germany) providing an inert gas atmosphere to prevent the hydration of KHF_2 upon exposure to moisture. The mixture was transferred into a platinum capsule which was subsequently inserted into a boron nitride crucible (Henze Boron Nitride Products AG, Lauben, Germany). This crucible was finally placed into an 18/11 assembly. Details on the

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assembly are described in the literature [21–23]. The assembly was then inserted into the middle of eight tungsten carbide cubes (Hawedia, Marklkofen, Germany) which transfer the pressure from six steel wedges to the 18/11 assembly and to the sample. A 1000 t multi-anvil press (Max Vöggenreiter GmbH, Mainleus, Germany) ensures the compression of the sample *via* a Walker-type module, which includes the steel wedges and the tungsten carbide cubes.

The sample was compressed within 65 min to 2.5 GPa and held at that pressure during the following heating program. The sample was then heated to 350 °C within 10 min, held at that temperature for further 60 min, and cooled down to room temperature within 40 min. After the end of the heating program, the sample was decompressed to room pressure within 200 min. A colorless, crystalline sample was recovered. It is mandatory to open the sample under inert gas atmosphere, as the substance is hygroscopic.

In a second step, doping of K_2SnOF_4 with Mn^{4+} was achieved by a ball-milling process. For this step, 70 mg (0.24 mmol) K_2SnOF_4 , 2.6 mg (0.01 mmol) K_2MnF_6 , and 200 mg ZrO_2 milling balls ($\varnothing = 1$ mm) were weighed in under argon atmosphere and transferred into a zirconia vessel. The milling process of 6×10 min at 300 rpm (15 min breaks between the steps) was carried out in a planetary mill (Pulverisette 7, FRITSCH, Idar-Oberstein, Germany).

$K_2WO_3F_2$ was also synthesized *via* a high-pressure/high-temperature route. The starting materials KF and WO_3 were ground together under inert gas atmosphere and subsequently transferred into a platinum capsule. The capsule was placed into a boron nitride crucible, which was subsequently inserted into an 18/11 assembly. The assembly was placed into the multi-anvil set-up as described above.

Compression of the sample to 5.5 GPa took 145 min. This pressure was kept during the following heating program. The sample was heated to 900 °C within 10 min, kept at that temperature for 60 min and slowly cooled to 350 °C within 30 min. Afterwards the sample was decompressed to ambient pressure within 430 min. A colorless and crystalline product was recovered.

2.2 X-ray analysis

A STOE Stadi P powder diffractometer was used to collect the diffraction data of the powder sample in the 2θ range of 2.0–40.4° and with a step size of 0.015°. The instrument is equipped with a Mythen 2 DCS4 detector, a Ge(111) primary beam monochromator, and a molybdenum radiation source $MoK\alpha_1$ ($\lambda = 70.93$ pm). The data was recorded at room temperature.

For the structure analysis, single crystals were isolated under a polarization microscope and mounted onto a sample holder. For data collection, a Bruker D8 Quest diffractometer was used (BRUKER, Billerica, USA). The crystal of K_2SnOF_4 was cooled to 173(2) K and the crystal of $K_2WO_3F_2$ was cooled to 183(2) K during the measurements. The diffractometer was equipped with an Incoatec micro-focus X-ray tube (Incoatec, Geesthacht, Germany) using $MoK\alpha$ radiation ($\lambda = 71.07$ pm). Collection of the intensity data was accomplished by a Photon 100 detector. A multi-scan absorption correction was applied, using SADABS 2014/5. For K_2SnOF_4 , the space groups $Pna2_1$ (no. 33) and $Pnma$ (no. 62) were considered for the structure solution with SHELXTL-XT-2014/4 on the basis of the extinction conditions. The space group $Pnma$ (no. 62) was found to be correct during the refinement. The WinGX-2013.3 [24] suite was used to carry out the parameter refinement (full-matrix least-squares against F^2) with SHELXL-2013 [25, 26].

For $K_2WO_3F_2$, the space groups $Pna2_1$ (no. 33) and $Pnma$ (no. 62) were considered for the structure solution (SHELXTL-XT-2014/4), and $Pnma$ (no. 62) was found to be correct during the refinement. The WinGX-2013.3 [24] suite was used to carry out the parameter refinement (full-matrix least-squares against F^2) with SHELXL-2013 [25, 26].

Further information on the crystal structure investigations can be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the deposition number CCDC 2019752 for K_2SnOF_4 , and CCDC 2019753 for $K_2WO_3F_2$.

2.3 EDX-spectroscopy

The chemical composition was analyzed by energy dispersive X-ray spectroscopy (EDX) using a SUPRATM35 scanning electron microscope (SEM, CARL ZEISS, Oberkochen, Germany, field emission) equipped with a Si/Li EDX detector (OXFORD INSTRUMENTS, Abingdon, Great Britain, model 7426).

2.4 Vibrational spectroscopy

A Bruker Alpha-P spectrometer (BRUKER, Billerica, USA), equipped with a DTGS detector and a 2×2 mm diamond ATR crystal, was used for the characterization of K_2SnOF_4 and $K_2WO_3F_2$ by FT-IR-ATR (Attenuated Total Reflection) spectroscopy. The handling of the data was carried out using the OPUS 7.2 software.

2.5 Luminescence spectroscopy

$K_2SnOF_4:Mn^{4+}$ was excited by a blue light laser diode (THORLABS, Newton, USA) with a wavelength of $\lambda = 448$ nm. The emission spectrum was recorded using a CCD-Detector (AVA AvaSpec 2048, AVANTES, Apeldoorn, The Netherlands). To ensure proper measurements, the set-up was calibrated for spectral radiance prior to the experiments using a tungsten-halogen calibration lamp. The software AVA AVASOFT full version 7 was used for data handling.

3 Results and discussion

3.1 Crystal structure of K_2SnOF_4

K_2SnOF_4 crystallizes in the orthorhombic crystal system with space group $Pnma$ (no. 62). It is isostructural to $(NH_4)_2FeF_5$ and its lattice parameters are 612.4(1), 738.4(1), and 1082.9(1) pm for a , b , and c , respectively [27]. The volume of the unit cell of K_2SnOF_4 amounts to 0.4896(1) nm³ with 32 atoms comprised by four formula units. The asymmetric unit is formed by one tin, two potassium, one oxygen, and two fluorine atoms. Tin is located at the special Wyckoff site $4a$, both potassium as well as the oxygen positions are located at $4c$, and the two fluorine positions are located at general Wyckoff sites $8d$. Therefore, the Wyckoff sequence of K_2SnOF_4 is d^2c^3a and the Pearson code is $oP32$.

Information on the crystal structure refinement can be found in Table 1. The atomic coordinates and displacement parameters, as well as selected distances and angles can be found in Tables S1–S4 (Supporting Information available online).

The main structural motif of K_2SnOF_4 is an $[SnO_2F_4]^{4-}$ octahedron (Figure 1, left). Within this octahedron, the Sn–F bond lengths are 201.0(1) and 202.1(1) pm for Sn1–F1 and Sn1–F2, respectively, whereas the Sn–O bond length is 196.7(1) pm (Table S3; Supporting Information). These bond lengths are in accordance to the ones reported in the literature for $K_5Sn_2OF_{11}$ ($d_{Sn-F} = 196.4(6)$ – $200.3(4)$ pm; $d_{Sn-O} = 194.7(3)$ – $195.3(2)$ pm) [19]. The bond angles confirm an octahedral coordination sphere (Table S4; Supporting Information).

The octahedra are interconnected *via* common oxygen atoms (O1) and build infinite chains along [010] (Figure 1, right). The Sn1–O1–Sn1 tilting angles are approx. 140°. These chains are quasi isolated from each other through potassium cations. Within the structure, there are two

Table 1: Crystal data and structure refinement of K_2SnOF_4 and $K_2WO_3F_2$.

Empirical formula	K_2SnOF_4	$K_2WO_3F_2$
Molar mass, g mol ^{−1}	288.89	348.05
Crystal system	orthorhombic	orthorhombic
Space group	$Pnma$ (no. 62)	$Pnma$ (no. 62)
Powder data		
Powder diffractometer	STOE Stadi P	
Radiation/wavelength λ , pm	MoK α_1 /70.93	
Temperature, K	293(2)	293(2)
a , pm	615.14(4)	610.83(4)
b , pm	739.02(5)	736.40(3)
c , pm	1086.82(7)	1081.47(7)
V , nm ³	0.49407(6)	0.48647(5)
Single-crystal data		
Single-crystal diffractometer	Bruker D8 Quest Photon 100	
Radiation/wavelength λ , pm	MoK α /71.07	
a , pm	612.35(2)	607.71(3)
b , pm	738.35(3)	735.19(3)
c , pm	1082.94(5)	1077.38(5)
V , nm ³	0.4896(1)	0.4814(1)
Formula units per cell, Z	4	4
Calculated density, g cm ^{−3}	3.92	4.80
Temperature, K	173(2)	183(2)
Absorption coefficient, mm ^{−1}	6.9	25.7
$F(000)$, e	528	616
2θ range, deg	6.7–75.7	6.7–70.0
Range in hkl	$\pm 10, \pm 11, \pm 18$	$\pm 9, \pm 11, \pm 17$
Total no. of reflections	13105	16518
Independent refl./ ref. param./ R_{int}	1401 / 44 / 0.0309	1123 / 58 / 0.0449
Reflections with $I > 2\sigma(I)$	1205	1013
Goodness-of-fit on F_i^2	1.065	1.163
Absorption correction	Semi-empirical (from equivalents)	
Final $R1/wR2$ ($I \geq 2\sigma(I)$)	0.0153 / 0.0377	0.0148 / 0.0335
Final $R1/wR2$ (all data)	0.0205 / 0.0397	0.0179 / 0.0343
Largest diff. Peak/hole, $e \text{ \AA}^{-3}$	0.83 / −0.81	0.71 / −0.50

crystallographically different potassium atoms. Both are nine-fold coordinated by eight fluorine atoms and one oxygen atom. The K–F bond lengths vary between 268.1(1) and 271.4(1) pm, the K–O bonds are 276.7(2) and 288.3(2) pm for K1–O1 and K1–O2, respectively. The coordination spheres of both potassium cations are depicted in Figure 2. A unit cell of K_2SnOF_4 is shown in Figure 3.

Bond-length/bond-strength (BLBS) and charge-distribution calculations (CHARDI, program CHARDI2015) confirmed the structural model (Table S5; Supporting Information) [28–31]. EDX measurements proved the cation composition of K_2SnOF_4 to be 2:1.2(2) for the ratio potassium to tin. An SEM image of a polycrystalline sample of K_2SnOF_4 is shown in Figure S1 (Supporting Information).

K_2SnOF_4 was synthesized as the main phase but not phase pure. Analysis *via* the Rietveld technique

Figure 1: $[SnO_2F_4]^{4-}$ octahedron (left) and infinite chain of octahedral units (right).

Figure 2: Coordination spheres of K1 (left) and K2 (right), with bond lengths given in pm.

determined the powder composition to be 70(2) wt% K_2SnOF_4 with SnO_2 (4(1) wt%), KHF_2 (26(2) wt%), and an unknown substance as side-phases (Figure 4).

3.2 Crystal structure of $K_2WO_3F_2$

$K_2WO_3F_2$ crystallizes in the orthorhombic crystal system with space group $Pnma$ (no. 62). Its crystal structure is isostructural to the one of K_2SnOF_4 described above. The lattice parameters of $K_2WO_3F_2$ are 607.71(3), 735.19(3), and 1077.38(5) pm for a , b , and c , respectively. Its cell volume is 0.4814(1) nm³. Within the $K_2WO_3F_2$ structure there are seven crystallographically different positions. These are two tungsten positions W1 and W2 at Wyckoff site 8d with an occupancy of 0.25 each. Additionally, there are two fully occupied potassium positions K1 and K2 at the Wyckoff site 4c. A fully occupied oxygen position is located at Wyckoff site 4c, and two positions exhibiting a mixed occupancy of oxygen and fluorine (1:1) are located at Wyckoff site 8d. Therefore, the Wyckoff sequence of $K_2WO_3F_2$ is d^4c^3 . The

unit cell consists of four formula units, which amounts to 32 atoms. This leads to the Pearson code $oP32$.

Information on the crystal structure refinement can be found in Table 1. Atomic coordinates, anisotropic displacement parameters, as well as important distances and angles are listed in Tables S6–S9 (Supporting Information).

The main motif of the crystal structure is an octahedral $[WO_4F_2]^{4-}$ unit (Figure 5, left). Within this unit, tungsten is shifted from the central position in the direction of the equatorial oxygen atoms. Since these equatorial positions exhibit a statistical disorder of oxygen and fluorine (1:1), the deflection of tungsten in the direction of the oxygen atoms from the Wyckoff site 4a to the site 8d introduces four possible locations for tungsten within this unit (Figure 5, right top). This leads to the assumption that the *cis*-conformation of fluorine is observed more often than the *trans*-conformation (Figure 5, right bottom), which would not deflect tungsten from the center of the octahedral unit. A *cis*-conformation is also observed for the two compounds $Cs_2WO_3F_2$ and $Ba_2WO_3F_4$ [2, 8, 10]. The W–O

Figure 3: Unit cell projection of K_2SnOF_4 along $[100]$ (top) and along $[010]$ (bottom).

bond lengths are shorter in comparison to the W–F bond lengths due to the deflection of tungsten. This is consistent with literature data, describing shorter bond lengths for W–O than for W–F, e.g., within the compound $Ag(WOF_5)_2$ ($d_{W-O} = 172.2$ to 177.2 pm; $d_{W-F} = 182.6$ to 207.5 pm), which is likely a result of the more covalent bonding character of

tungsten and oxygen in comparison to tungsten and fluorine [9].

The octahedral units are connected *via* common oxygen atoms and form chains along $[010]$ (Figure 6, left). Within the chain, the octahedra are tilted towards each other with a tilting angle (W–O–W) of approx. 149° (Figure 6, right). These chains are quasi-isolated by potassium cations, which occupy two crystallographically independent positions (Figure 6, left). The coordination spheres of the two potassium cations are shown in Figure 7. Both are coordinated nine-fold by eight mixed O/F positions and one oxygen position. The K–O bond lengths are $289.6(1)$ and $294.6(1)$ pm, whereas the K–O/F lengths vary from $271.7(1)$ to $312.0(1)$ pm. The mixed occupancy of the fluorine and oxygen positions as well as the deflection of tungsten hints at the possibility that this phase is a high-temperature modification. At low temperatures, an ordering of the structures might be possible, although no signs of ordering were observed down to $T = 183(2)$ K.

EDX analysis confirmed the atomic ratio of K:W to $1.9(1):1$ for $K_2WO_3F_2$. An SEM image of a polycrystalline sample is shown in Figure S2 (Supporting Information). Phase analysis *via* the Rietveld technique led to $K_2WO_3F_2$ as main product with small amounts of an unknown side phase present (Figure 8).

3.3 Vibrational spectroscopy

3.3.1 FT-IR spectrum of K_2SnOF_4

IR bands for the compound K_2SnOF_4 were reported in 1963 by Kolditz und Preiss [20]. They observed a strong absorption band at 442 cm^{-1} , as well as two very strong bands at 490 and 532 cm^{-1} . These three absorption bands are also found for the sample prepared during this work (448 , 487 , and 520 cm^{-1}). Kolditz und Preiss also observed bands at

Figure 4: Plot of the powder analysis *via* the Rietveld method. The experimental powder pattern is plotted with black crosses, the calculated curve as the red solid line and the difference curve as the blue solid line. Reflection positions of K_2SnOF_4 , SnO_2 and KHF_2 are shown as black tick marks in the top, middle and bottom rows, respectively. Reflections belonging to an unknown side phase are marked with purple asterisks.

Figure 5: Octahedral $[WO_4F_2]^{4-}$ unit (left), possible *cis*-conformation (right, top) and possible *trans*-conformations (right, bottom). The bond lengths are given in pm.

Figure 6: Central projection of the unit cell of $K_2WO_3F_2$ along $[100]$ (left-top) and along $[010]$ (left-bottom). A chain of $[WO_4F_2]^{4-}$ units is shown on the right.

Figure 7: Coordination sphere of K1 (left) and K2 (right).

755 and 820 cm^{-1} . In contrast to their work, these bands are absent for our sample (Figure 9), but a medium strong absorption band can be noticed at 783 cm^{-1} . Another quite

broad, but weak absorption band, located at 1590 cm^{-1} , as well as two weak but sharp absorption bands (1181 and 1122 cm^{-1}) likely belong to KHF_2 (unreacted starting

Figure 8: Phase analysis via the Rietveld technique. The black curve shows the measured pattern, the red curve the calculated one, and the blue line marks the difference curve. The black tick marks correspond to the hkl positions of $K_2WO_3F_2$. Purple asterisks mark reflections belonging to an unknown side phase.

material) [32]. Lastly, some very weak but sharp absorption bands are located at 618 and 644 cm^{-1} . These bands might be due to the unknown side phase. Above 1600 cm^{-1} , no absorption bands are noticeable, suggesting that no O–H bonds were overlooked during the structure determination by X-ray diffraction.

3.3.2 FT-IR spectrum of $K_2WO_3F_2$

The FT-IR spectrum of $K_2WO_3F_2$ in the range of 400 to 4000 cm^{-1} is shown in Figure 10. No bands above 1500 cm^{-1} are noticeable; therefore, the structure does not contain any water. In analogy to $Cs_2WO_3F_2$ and $(NH_4)_2MoO_3F_2$, the bands at around 920 cm^{-1} , 850 cm^{-1} , and 800 cm^{-1} can be attributed to W–O bonds [8, 33]. The bands resulting of the W–F bonds are expected below 500 cm^{-1} [8, 33]. Similar data have been reported for $Ba_2WO_3F_4$, confirming similar

structural motifs in $Ba_2WO_3F_4$, $Cs_2WO_3F_2$, and $K_2WO_3F_2$ [10].

4 Luminescence spectroscopy

Partial substitution of the central Sn^{4+} ($r_{Sn} = 0.83 \text{ \AA}$; CN = 6) cation by Mn^{4+} ($r_{Mn} = 0.67 \text{ \AA}$; CN = 6) via a ball-milling step was achieved for K_2SnOF_4 . A comparison of a powder pattern before and after the ball-milling process is depicted in Figure S3 (Supporting Information). No change in the powder pattern before and after the process is noticeable; therefore the powder composition does not change and still contains K_2SnOF_4 as the main phase. We suspect that the substitution of Sn^{4+} with Mn^{4+} likely takes place at the surface of the crystal during the ball-milling process. The emission spectrum of $K_2SnOF_4:Mn^{4+}$ is depicted in Figure 11. It shows a line emission spectrum with broader

Figure 9: FT-IR spectrum of K_2SnOF_4 in the range of 400–4000 cm^{-1} .

Figure 10: FT-IR spectrum of $K_2WO_3F_2$ in the range of 400–4000 cm^{-1} .

Figure 11: Emission spectrum of K_2SnOF_4 by excitation with a blue laser $\lambda_{exc} = 448$ nm in comparison to the emission spectra of $K_2SiF_6:Mn^{4+}$ and K_2MnF_6 .

lines compared to K_2SiF_6 . There are several reasons that might result in a broadening of the emission lines. This could be due to the ball-milling process itself, which induces local deformations on the surface of the crystals, where the substitution should take place. This may result in a broad range of activator-ligand distances, which slightly affect the peak position also for $d-d$ transitions. Alternatively, it might be attributed to small distortions of the local symmetry around the manganese cation, either induced again by the surface deformation or by O/F disorder. The origin may also be a temperature-induced effect, which leads to a broadening of the lines, when the material is heated. We do not suspect the first two mechanisms as the main factor, but the third to be the main reason of the broadening, as described for $Cs_2WO_2F_4$ [6]. A non-radiant transition during the measurement can lead to an internal heating of the material and therefore influence the emission properties. Altogether seven emission lines are visible, which can be attributed to the spin and parity forbidden $d-d$ transitions. In detail, the lines at approx. 598, 609, 613, 622, 631, 634, and 647 nm correspond to the transition of the vibronic modes $\nu_3(t_{1u})$, $\nu_4(t_{1u})$, $\nu_6(t_{2u})$, ZPL, $\nu_6(t_{2u})$, $\nu_4(t_{1u})$, and $\nu_3(t_{1u})$, respectively. As a result of the distorted coordination sphere around the tin atom, the ZPL is visible. The small amount of sample, as well as a low emission intensity hindered further characterization of the material.

5 Conclusion

K_2SnOF_4 and $K_2WO_3F_2$ crystallize in the orthorhombic crystal system with crystal structures that are isostructural to the one

of $(NH_4)_2FeF_5$ [27]. Main motifs are an octahedral $[SnO_2F_4]^{4-}$ unit for K_2SnOF_4 and an octahedral $[WO_4F_2]^{4-}$ unit for $K_2WO_3F_2$, which exhibits a disorder on the tungsten site and a mixed O/F occupancy around the equatorial positions. Within the structures, these units form infinite chains and these chains in turn are quasi-isolated by potassium cations. It is quite surprising that these two structures are similar to each other, as the central cations exhibit different oxidation states. These differences in the oxidation state are compensated by a change in the oxygen to fluorine ratio around the central cation, leading to the formation of the same structure motif. Both substances were synthesized as the main phases but not phase-pure. FT-IR spectra show the absence of water within the structures and therefore confirm the structural models. The similarity of the structural motif of $K_2WO_3F_2$ with the ones of $Cs_2WO_3F_2$ and $Ba_2WO_3F_4$ were confirmed by a comparison of the location and intensity of the bands in the FT-IR spectra. Upon partial substitution of Mn^{4+} on the Sn^{4+} site, an emission spectrum of $K_2SnOF_4:Mn^{4+}$ can be detected. The line with maximum intensity is located at $\lambda_{max} \approx 631$ nm. Therefore, oxidofluoridometallates are a highly interesting class of compounds which are suitable for doping with Mn^{4+} . Additionally, it offers a great structural variety and gives us the chance to study the emission behavior of Mn^{4+} in different environments. If it is possible to increase the quantity of the sample as well as the luminous intensity of the product by optimization of the synthesis process, temperature dependent emission spectra would give an insight into the mechanism of the thermal quenching behavior of interconnected octahedral units, which might lead to higher thermal stability.

6 Supporting information

Atomic coordinates, displacement parameters, interatomic distances and angles and SEM images of polycrystalline samples of K_2SnOF_4 and $K_2WO_3F_2$ as well as the charge contributions according to the bond-valence sums and the CHARDI concept for K_2SnOF_4 and a comparison of the powder XRD patterns of K_2SnOF_4 before and after the ball-milling process are given as supplementary material available online (<https://doi.org/10.1515/znbn-2020-0132>).

Acknowledgments: We want to express our gratitude to Assoc.-Prof. Dr. Gunter Heymann for the collection of the single-crystal data and to Dr. Klaus Wurst for the help with the crystal structure refinement. We also want to thank Christian Koch for the EDX and SEM measurements.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Leblanc M., Maisonneuve V., Tressaud A. *Chem. Rev.* 2015, 115, 1191–1254.
2. Torardi C. C., Brixner L. H. *Mater. Res. Bull.* 1985, 20, 137–145.
3. Peraudeau G., Ravez J., Hagenmuller P. *Solid State Commun.* 1978, 27, 591–593.
4. Stoll C., Heymann G., Seibald M., Baumann D., Huppertz H. *J. Fluor. Chem.* 2019, 226, 109356; <https://doi.org/10.1016/j.jfluchem.2019.109356>.
5. Molokeev M. S., Misyul S. V., Fokina V. D., Kocharova A. G., Aleksandrov K. S. *Phys. Solid State* 2011, 53, 834–839.
6. Cai P., Qin L., Chen C., Wang J., Seo H. *J. Dalton Trans.* 2017, 46, 14331–14340.
7. Hu T., Lin H., Cheng Y., Huang Q., Xu J., Gao Y., Wang J., Wang Y. *J. Mater. Chem. C* 2017, 5, 10524–10532.
8. Mattes R., Förster H. *Z. Anorg. Allg. Chem.* 1982, 494, 109–114.
9. Mazej Z., Gilewski T., Goresnik E. A., Jaglicic Z., Derzsi M., Grochala W. *Inorg. Chem.* 2017, 56, 224–233.
10. Wingfeld G., Hoppe R. *Z. Anorg. Allg. Chem.* 1984, 518, 149–160.
11. Udovenko A. A., Laptash N. M. *Acta Crystallogr.* 2008, B64, 645–651.
12. Srivastava A. M., Ackerman J. F. *J. Solid State Chem.* 1992, 98, 144–150.
13. Tucker P. A., Taylor P. A., Holloway J. H., Russell D. R. *Acta Crystallogr.* 1975, B31, 906–908.
14. Adachi S. *J. Lumin.* 2020, 218, 116829.
15. Cai P., Wang X., Seo H. *J. Phys. Chem. Chem. Phys.* 2018, 20, 2028–2035.
16. Hu T., Lin H., Gao Y., Xu J., Wang J., Xiang X., Wang Y. *J. Am. Ceram. Soc.* 2018, 101, 3437–3442.
17. Jansen T., Funke L. M., Gorobez J., Böhnisch D., Hoffmann R.-D., Heletta L., Pöttgen R., Hansen M. R., Jüstel T., Eckert H. *Dalton Trans.* 2019, 48, 5361–5371.
18. Stoll C., Seibald M., Baumann D., Huppertz H. *Eur. J. Inorg. Chem.* 2019, 29, 3383–3388.
19. Stoll C., Seibald M., Huppertz H. *Z. Naturforscher* 2019, 75b, 83–90.
20. Kolditz L., Preiss H. *Z. Anorg. Allg. Chem.* 1963, 325, 263–274.
21. Huppertz H. *Z. Kristallogr.* 2004, 219, 330–338.
22. Walker D., Carpenter M. A., Hitch C. M. *Am. Mineral.* 1990, 75, 1020–1028.
23. Walker D. *Am. Mineral.* 1991, 76, 1092–1100.
24. Farrugia L. J. *J. Appl. Crystallogr.* 2012, 45, 849–854.
25. Sheldrick G. M. *Acta Crystallogr.* 2008, A64, 112–122.
26. Sheldrick G. M. *Acta Crystallogr.* 2015, C71, 3–8.
27. Croguennec L., Deniard P., Brec R., Couzi M., Sourisseau C., Fourquet J. L., Calage Y. *J. Solid State Chem.* 1997, 131, 189–197.
28. Brese N. E., O’Keeffe M. *Acta Crystallogr.* 1991, B47, 192–197.
29. Brown I. D., Altermatt D. *Acta Crystallogr.* 1985, B41, 244–247.
30. Hoppe R., Voigt S., Glaum H., Kissel J., Müller H. P., Bernet K. *J. Less Common. Met.* 1989, 156, 105–122.
31. Nespolo M., Guillot B. *J. Appl. Crystallogr.* 2016, 49, 317–321.
32. Ketelaar J. A. A., Vedder W. *J. Chem. Phys.* 1951, 19, 654.
33. Mattes R., Müller G., Becher H. *J. Z. Anorg. Allg. Chem.* 1975, 416, 256–262.

Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/znb-2020-0132>).