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K₂SnOF₄ and K₂WO₃F₂ – different but similar

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Abstract: K₂SnOF₄ and K₂WO₃F₂ 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 orthorhombic crystal system with space group Pnma and are isostructural to each other. The main motifs of the structures are octahedral [SnO₂F₄]⁴⁻ and [WO₄F₂]⁴⁻ entities for K₂SnOF₄ and K₂WO₃F₂, 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 K₂SnOF₄ with Mn⁴⁺ yielded a red phosphor material which was analyzed by luminescence spectroscopy. The emission maximum is located at λ_{max} = 631 nm.

Keywords: crystal structure; potassium oxidofluoridotannate; 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 are contained within these units, as well as other oxidofluoridometallates exhibiting similar units, recently gained some attention because of the possibility for partial substitution with Mn⁴⁺ which can produce materials exhibiting red luminescence upon blue light excitation [6–7, 14–18]. Regarding the [WO₄F₂]⁴⁻ unit, which has been observed within the compound Cs₂WO₃F₂ by Mattes and Förster, and within Ba₂WO₃F₄ 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 [SnO₂F₄]⁴⁻ unit has been reported in the literature. It has been observed in the structure of K₃Sn₂OF₁₁ [19], where this unit forms quasi-isolated dinuclear motifs. [19]. Even though the [SnO₂F₄]⁴⁻ unit was predicted for the compound K₂SnOF₄ by Kolditz and Preiss, this assumption has not yet been confirmed [20].

Therefore, we took the chance to analyze the crystal structures of K₂SnOF₄ and K₂WO₃F₂, exhibiting [SnO₂F₄]⁴⁻ and [WO₄F₂]⁴⁻ units, respectively, by means of single-crystal structure determination.

2 Experimental section

2.1 Synthesis

K₂SnOF₄ was synthesized from SnO₂ and KHF₂ 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 KHF₂ 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 structure determination are to be published elsewhere.

The emission maximum is located at λ_{max} = 631 nm.
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 Voggenreiter 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\textsubscript{2}SnOF\textsubscript{4} with Mn\textsuperscript{4+} was achieved by a ball-milling process. For this step, 70 mg (0.24 mmol) K\textsubscript{2}SnOF\textsubscript{4}, 2.6 mg (0.01 mmol) K\textsubscript{2}MnF\textsubscript{6}, and 200 mg ZrO\textsubscript{2} milling balls (Ø = 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\textsubscript{2}WO\textsubscript{3}F\textsubscript{2} was also synthesized via a high-pressure/high-temperature route. The starting materials KF and WO\textsubscript{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. 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\textsubscript{2}SnOF\textsubscript{4} was cooled to 173(2) K and the crystal of K\textsubscript{2}WO\textsubscript{3}F\textsubscript{2} was cooled to 183(2) K during the measurements. The diffractometer was equipped with an Incoatec microfocus X-ray tube (Incoatec, Geesthacht, Germany) using MoK\textalpha radiation (λ = 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\textsubscript{2}SnOF\textsubscript{4}, the space groups Pna\textsubscript{2} (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\textsuperscript{2}) with SHELXL-2013 [25, 26].

For K\textsubscript{2}WO\textsubscript{3}F\textsubscript{2}, the space groups Pna\textsubscript{2} (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\textsuperscript{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\textsubscript{2}SnOF\textsubscript{4}, and CCDC 2019753 for K\textsubscript{2}WO\textsubscript{3}F\textsubscript{2}.

2.3 EDX-spectroscopy

The chemical composition was analyzed by energy dispersive X-ray spectroscopy (EDX) using a SUPRA\textsuperscript{35} 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\textsubscript{2}SnOF\textsubscript{4} and K\textsubscript{2}WO\textsubscript{3}F\textsubscript{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$_2$SnOF$_4$:Mn$^{+1}$ 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 setup 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$_2$SnOF$_4$

K$_2$SnOF$_4$ crystallizes in the orthorhombic crystal system with space group Pnma (no. 62). It is isosstructural to (NH$_4$)$_2$FeF$_6$ 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$_2$SnOF$_4$ amounts to 0.4896(1) nm$^3$ 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$_2$SnOF$_4$ 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$_2$SnOF$_4$ is an [SnO$_2$F$_4$]$^{4-}$ 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$_2$Sn$_2$O$_7$F$_4$ (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 (01) 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 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$_2$SnOF$_4$ is shown in Figure 3.

| Table 1: Crystal data and structure refinement of K$_2$SnOF$_4$ and K$_2$WO$_3$F$_2$. |
|-----------------------------------------------|
| Empirical formula | K$_2$SnOF$_4$ | K$_2$WO$_3$F$_2$ |
| 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 $\lambda$, pm | MoK$_\alpha_1/170.93$ | MoK$_\alpha_1/71.07$ |
| 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) |
| $\nu$, nm$^3$ | 0.49407(6) | 0.48647(5) |
| Single-crystal data | Single-crystal diffractometer | Bruker D8 Quest Photon 100 |
| Radiation/wavelength $\lambda$, pm | MoK$_\alpha_1/71.07$ | MoK$_\alpha_1/170.93$ |
| a, pm | 612.35(2) | 607.71(3) |
| b, pm | 738.35(3) | 735.19(3) |
| c, pm | 1082.94(5) | 1077.38(5) |
| $\nu$, nm$^3$ | 0.4896(1) | 0.4814(1) |
| 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 |
| 2$\theta$ range, deg | 6.7–75.7 | 6.7–70.0 |
| Range in $hkl$ | ±10, ±11, ±18 | ±9, ±11, ±17 |
| Total no. of reflections | 13105 | 16518 |
| Independent refl./ref. param./R$_{int}$ | 1401 / 44 / 0.0309 | 1123 / 58 / 0.0449 |
| Reflections with $l > 2 \sigma(l)$ | 1205 | 1013 |
| Goodness-of-fit on $F^2$ | 1.065 | 1.163 |
| Absorption correction | Semi-empirical (from equivalents) | |
| Final R1/wR2 ($l > 2 \sigma(l)$) | 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 Å$^{-3}$ | 0.83 / −0.81 | 0.71 / −0.50 |
determined the powder composition to be 70(2) wt% K₂SnOF₄ with SnO₂ (4(1) wt%), KHF₂ (26(2) wt%), and an unknown substance as side-phases (Figure 4).

### 3.2 Crystal structure of K₂WO₃F₂

K₂WO₃F₂ crystallizes in the orthorhombic crystal system with space group Pnma (no. 62). Its crystal structure is isostructural to the one of K₂SnOF₄ described above. The lattice parameters of K₂WO₃F₂ 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 K₂WO₃F₂ 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 K₂WO₃F₂ is d⁶c⁵. 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 [WO₄F₂]⁻⁻ 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 Cs₂WO₃F₂ and Ba₂WO₃F₄ [2, 8, 10]. The W–O...
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$_2$WO$_3$F$_2$. An SEM image of a polycrystalline sample is shown in Figure S2 (Supporting Information). Phase analysis via the Rietveld technique led to K$_2$WO$_3$F$_2$ 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$_2$SnOF$_4$

IR bands for the compound K$_2$SnOF$_4$ 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 3: Unit cell projection of K$_2$SnOF$_4$ along [100] (top) and along [010] (bottom).](image)

![Figure 4: Plot of the powder analysis via the Rietveld method.](image)
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
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\(_2\)WO\(_3\)F\(_2\)

The FT-IR spectrum of K\(_2\)WO\(_3\)F\(_2\) 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\(_2\)WO\(_3\)F\(_2\) and (NH\(_4\))\(_2\)MoO\(_3\)F\(_2\), 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\(_2\)WO\(_3\)F\(_4\), confirming similar structural motifs in Ba\(_2\)WO\(_3\)F\(_4\), Cs\(_2\)WO\(_3\)F\(_2\), and K\(_2\)WO\(_3\)F\(_2\) [10].

### 4 Luminescence spectroscopy

Partial substitution of the central Sn\(^{4+}\) (\(r_{\text{Sn}} = 0.83\ \text{Å}; \text{CN} = 6\)) cation by Mn\(^{4+}\) (\(r_{\text{Mn}} = 0.67\ \text{Å}; \text{CN} = 6\)) via a ball-milling step was achieved for K\(_2\)SnOF\(_4\). 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\(_2\)SnOF\(_4\) 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\(_2\)SnOF\(_4\):Mn\(^{4+}\) is depicted in Figure 11. It shows a line emission spectrum with broader
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 $\nu_3(t_{1u})$, $\nu_4(t_{1u})$, $\nu_5(t_{2u})$, 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, oxido fluorometallates 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/znb-2020-0132).

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