

Systems of Potassium Oxofluorotantalates

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The formation of potassium oxofluorotantalates and potassium oxotantalates in the system $\text{KF}-\text{K}_2\text{TaF}_7-\text{Ta}_2\text{O}_5$ was investigated. A general reaction scheme was suggested based on the approach of “figurative points diagram”. Experimental testing of the reaction scheme revealed the stability of only certain potassium oxofluorotantalates. The summary of all known potassium oxofluorotantalates is given and some corrections of former data on existence of certain compounds are discussed.

Potassium oxotantalates and potassium oxofluorotantalates are interesting from theoretical as well as from practical point of view. They can crystallize in perovskite, tungsten bronze or defect pyrochlore’s type structure. Some of these compounds can be used as superconductors, piezoelectrics, ferroelectrics, or for fast ion transport. They may be interesting for electrochemistry or metallurgy [1–4].

Research on the fluoride systems based on tantalum has more than hundred years. However, not few controversial data can be found in the literature. For example, $\text{K}_3\text{TaO}_2\text{F}_4$ was reported as cubic [5] and as tetragonal [6] both based on XRD or $\text{KTa}_2\text{O}_5\text{F} \cdot \text{H}_2\text{O}$ compound was reported as cubic with the property of reversible water molecule replacement [4] while elsewhere anhydrous compound $\text{KTa}_2\text{O}_5\text{F}$ was reported as tetragonal [7] with the cell parameters almost identical with those for $\text{K}_6\text{Ta}_{10.8}\text{O}_{30}$ [3]. The most frequently discussed anionic elements in inorganic molten systems are TaOF_6^{3-} , TaOF_5^{2-} , and $\text{TaO}_2\text{F}_4^{3-}$ [8–10]. It seems that suggestions of some chemical reaction or reaction products are not consistent.

Majority of potassium oxofluorotantalates are reported with tantalum in oxidation state (V). Also some peroxy compounds are known [11, 12]. $\{\text{TaOF}_5\}$ may serve as counter anion in more complicated complexes containing organic ligands as well [13–15].

In this work the summary of all known potassium oxofluorotantalates is given. The aim of this work is to initiate a discussion in the alternative treatment of complicated systems of molten salts. The demonstrative concepts will be shown on the system $\text{KF}-\text{K}_2\text{TaF}_7-\text{Ta}_2\text{O}_5$. In this system the formation of several potassium oxofluorotantalates was observed, but the system has not been elucidated satisfactorily. Systems containing K_2TaF_7 and Ta_2O_5 could be suitable

for electrochemical industry. Thus, the discussion may contribute to the optimization of the industrial efforts. The composition of any molten system has not been investigated in detail for any industrial process. Basic knowledge of the constituents and the amount of additional components was considered to be sufficient in order to obtain the requested product. In recent times efforts are going on to reveal the real compositions of melts in order to introduce new model reactions by computer techniques. Thus traditional trial and error methods may be overcome.

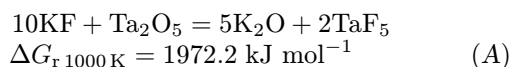
THEORETICAL

In general, if we consider potassium oxofluorotantalates of the formula $\text{K}_x\text{Ta}_y\text{O}_z\text{F}_a$ (with usual formal oxidation states of atoms; K(I), Ta(V), O(-II), F(-I)) we may generate theoretically plenty of possible compounds by simple variation of x , y , z , and a under the fulfilment of the condition of electroneutrality. Let us admit to say that more complicated compounds could be hypothetically composed from more basic ones (*e.g.* $\text{K}_3\text{Ta}_3\text{O}_4\text{F}_{10} = 2\text{KTaOF}_4 + \text{KTaO}_2\text{F}_2$).

It is obvious that not all compounds will exist. The possible formation depends on energy balance and steric properties. Only those with a mean coordination number lower than nine can be expected. Compounds with mean coordination number lower than six are expected to contain coordination polyhedra linked by bridges (oxygen or fluorine).

Now, let us consider the construction of the figurative points diagram in the reciprocal system $\text{KF}-\text{TaF}_5-\text{Ta}_2\text{O}_5-\text{K}_2\text{O}$. The “figurative points diagram” has the same coordinates as in the phase diagram but only figurative points are indicated as compounds of a defined composition. In the following we will use the

abbreviated term “diagram”. In this reciprocal system KF and Ta₂O₅ form the stable diagonal as



(value used for TaF₅ was extrapolated from 502 K).

Figurative points of potassium oxotantalates can be formed on the binary K₂O—Ta₂O₅ (e.g. K₂O + Ta₂O₅ = 2KTaO₃) and points of potassium fluorotantalates can be formed on the binary KF—TaF₅ (e.g. 2KF + TaF₅ = K₂TaF₇). We are not aware of any phase diagram of the system KF—K₂O but it is expected to be a simple eutectic system without forming any compounds. In the system Ta₂O₅—TaF₅ no phase diagram has been reported either but a formation of oxofluorotantalates TaOF₃ and TaO₂F can be expected. Moreover, these compounds are known. Figurative points of some potassium oxofluorotantalates can be formed from the compounds of the first stable triangle KF, TaF₅, and Ta₂O₅ (e.g. 5KF + TaF₅ + 2Ta₂O₅ = 5KTaO₂F₂). However, not all potassium oxofluorotantalates can be formed in this way. From the compounds of the second stable triangle K₂O, Ta₂O₅, and KF (e.g. Ta₂O₅ + K₂O + 2KF = 2K₂TaO₃F) also other potassium oxofluorotantalates can be constructed. Moreover, some of the potassium oxofluorotantalates can be situated on the binary KF and Ta₂O₅ (e.g. 3KF + Ta₂O₅ = K₃Ta₂O₅F₃).

The above discussion seems to be usable for solid state systems. It is obvious that electro-neutral potassium oxofluorotantalate compounds cannot be expected to be stable in the melt but only ionic entities will be present. Similarly we may generate possibly present ions. Probably higher charges will be unstable. Furthermore, it is obvious that only anions with mean coordination number lower than nine can be considered. These ions can react mutually. These reactions can be dissociation, association or substitution. A reaction scheme can be written e.g. TaF₇²⁻ → TaF₆⁻ + F⁻ for dissociation reaction; TaOF²⁺ + TaO₂F₂⁻ → Ta₂O₃F₃⁺ for association reaction; TaO₃F₂³⁻ + 2F⁻ → TaO₂F₄³⁻ + O²⁻ for substitution reaction.

Above concepts can serve as starting ideas for construction of expected interactions in the investigated system. However, some limitations must be noted.

i) There are almost no data in literature concerning Gibb's energies or enthalpies of above compounds. Thus majority of reactions are considered as just guide schemes or models.

ii) The degree of dissociation is difficult to predict.

iii) Further, if some oxofluorotantalate species may exist in the melt they may only be stable in the liquid phase and may decompose during crystallization.

iv) Boiling temperatures of electro-neutral species like TaOF₃, TaO₂F, and TaF₅ are several hundred degrees below the melting temperature of potassium oxotantalates and potassium oxofluorotantalates. Thus,

these compounds may volatilize and the equilibrium in the system will change. Hermetically closed system is the only way to solve this problem.

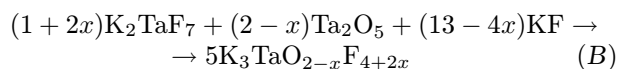
v) Potassium cations probably will not participate in the reactions but they may influence the reactions of remaining ions by their electrostatic potential and by polarizability properties.

vi) Mutual solubility of used components or formed products seems to be important parameter for estimating the phase composition in the system.

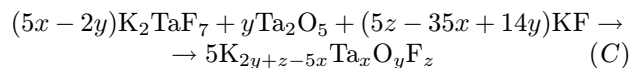
It is obvious that not all thought out compounds will be stable. It is the question of energy balance and steric properties. *Ab initio* calculation seems to be powerful tool to help us to predict the stability of certain ions and consequently to predict the formation of certain compounds after cooling of molten mixtures. Unfortunately, we are not aware of any calculation works in literature on such system, what may be a problem because of necessity to include relativistic effects.

The investigation of the system KF—K₂TaF₇—Ta₂O₅ is our concern.

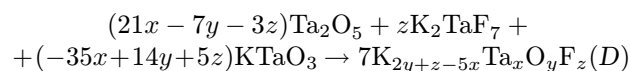
Fouad *et al.* [16] have proposed the general formula for preparation of certain potassium oxofluorotantalates (K₃TaO₂F₄ and K₃TaOF₆)



but we can extend this formula to the more general form



A similar reaction scheme can be written for any combination of three compounds that can provide certain potassium oxofluorotantalates, for example



as can be suggested from the results of *Chaminade et al.* [6], *Vlasse et al.* [17], *Boukhari et al.* [18]. Both eqns (C) and (D) are valid also for nonstoichiometric compounds like K₁₂Ta_{15.5}F_{18.5}O_{35.5} reported by *Boukhari et al.* [19] and K₆Ta_{6.5}O_{14.5}F_{9.5} by *Vlasse et al.* [20]. It should be noted that not all possible potassium oxofluorotantalates could be formed by these reactions.

In Table 1 a summary of all known potassium oxofluorotantalates is given. As can be seen, for most of them no complete structure determination has been reported and the formula is based on elemental analysis and X-ray powder data. Compounds that could obey eqn (C) are indicated by “*” sign. However, some of them were prepared by the reaction of other three starting compounds. The remaining compounds will probably obey other general equation.

Table 1. Known Potassium Oxofluorotantalates

Compound	Characterized by	Ref.
KTa ₂ O ₅ F see K ₆ Ta _{10.8} O ₃₀	XRD	[7]
KTa ₂ O ₅ F · H ₂ O	X – ICSD-9636	[4]
K _{0.15} Ta _{2.15} F _{0.85}	XRD – ICDD-23-0500	[21]
*K ₄ Ta ₂ O ₃ F ₁₂	XRD – ICDD-27-0441	[22]
*K _{0.4} Ta _{2.4} F _{0.6} see K ₆ Ta _{10.8} O ₃₀	XRD – ICDD-28-0805	[21]
*K ₃ TaO ₂ F ₄	XRD – ICDD-29-1051	[16, 6]
*K ₇ Ta ₁₂ O ₂₈ F ₁₁ (K _{2.33} Ta ₄ O _{9.33} F _{3.67})	XRD	[6]
*K ₃ TaOF ₆	XRD – ICDD-29-1052	[16, 6]
*K ₂ Ta ₄ O ₉ F ₄	X – ICSD-8204	[6, 18]
*K ₂ Ta ₂ O ₃ F ₆	X – ICSD-126	[23, 17]
*K ₁₂ Ta _{15.5} F _{18.5} O _{35.5}	X – ICSD-8229	[19]
*K ₆ Ta _{6.5} O _{14.5} F _{9.5}	X – ICSD-100188	[20]
*K ₆ Ta _{6.5} ^(4.85) O ₁₅ F _{7.56}	X – ICSD-93934	[24]
*K ₃ Ta ₄ F ₇ O ₈	X – ICSD-10430	[25]
K ₄ Ta ₄ O ₅ F ₁₄	-	[26, 27]
KTaOF ₄	-	[28]
K ₂ TaO ₃ F	-	[29]
*K ₂ TaO ₂ F ₃	-	[27]

*Compounds that could obey eqn (C); XRD – X-ray powder diffraction, X – X-ray single crystal analysis.

EXPERIMENTAL

In order to verify the validity of eqn (C) the following experiments were done. The mixtures of starting compounds (KF; 99.5 %, K₂TaF₇; min. 99 %, Ta₂O₅; 99.5 %) were melted under inert atmosphere in Pt cru-

cible at 1223 K for 1 h. Samples were slowly cooled and powdered. Then XRD patterns were recorded on Stoe Stadi P transmission diffractometer equipped with a curved Ge (111) monochromator placed in the primary beam and a linear PSD. In order to achieve a better resolution CuK α radiation was used. The records were taken in the 2 θ range of 7–90° at room temperature each for 6 h. Powdered samples were placed between acetate foils.

The experimental work is restricted to experiments with lower Ta₂O₅ mole fractions, because of its restricted solubility in KF. In Table 2 all these reactions are summarized.

RESULTS AND DISCUSSION

In Fig. 1 the summary of figurative points of known potassium oxofluorotantalates together with figurative points of compounds that we wanted to prepare is given. As can be seen the structure of oxofluorotantalates was solved only for compounds in the middle part of the diagram. Compounds K₆Ta_{6.5}F_{9.5}O_{14.5}, K₁₂Ta_{15.5}F_{18.5}O_{35.5}, and K₂Ta₄O₉F₄ belong to one structural family (hexagonal system). In these structures tantalum atoms are bridged by oxygen atoms forming certain rings. Remaining two compounds K₃Ta₄O₈F₇ and K₂Ta₂O₃F₆ have different structural motives. Compounds known only from XRD patterns are placed mainly in the bottom part of the diagram (K₃TaOF₆, K₄Ta₂F₁₂O, and K₃TaO₂F₄). The proposed compounds we wanted to prepare are placed between these two layers. Some of the proposed compounds are those that are mentioned in lit-

Table 2. Experimental Reactions of Ta₂O₅, K₂TaF₇, and KF according to Eqn (C)

Reaction	$x(\text{K}_2\text{TaF}_7)$	$x(\text{Ta}_2\text{O}_5)$	$x(\text{KF})$	Eqn
K ₂ TaF ₇ + 2Ta ₂ O ₅ + 3KF $\xrightarrow{\text{expected}}$ 5KTaO ₂ F ₂	16.67	33.33	50.00	(E)
3K ₂ TaF ₇ + Ta ₂ O ₅ + 4KF $\xrightarrow{\text{expected}}$ 5K ₂ TaOF ₅	37.50	12.50	50.00	(F)
K ₂ TaF ₇ + 2Ta ₂ O ₅ + 8KF $\xrightarrow{\text{expected}}$ 5K ₂ TaO ₂ F ₃	9.09	18.18	72.73	(G)
3K₂TaF₇ + Ta₂O₅ + 9KF $\xrightarrow{\text{expected}}$ 5K₃TaOF₆	23.08	7.69	69.23	(H)
K₂TaF₇ + 2Ta₂O₅ + 13KF $\xrightarrow{\text{expected}}$ 5K₃TaO₂F₄	6.25	12.50	81.25	(I)
3K ₂ TaF ₇ + Ta ₂ O ₅ + 14KF $\xrightarrow{\text{expected}}$ 5K ₄ TaOF ₇	16.67	5.56	77.78	(J)
K ₂ TaF ₇ + 2Ta ₂ O ₅ + 18KF $\xrightarrow{\text{expected}}$ 5K ₄ TaO ₂ F ₅	4.76	9.52	85.71	(K)
3K ₂ TaF ₇ + Ta ₂ O ₅ + 19KF $\xrightarrow{\text{expected}}$ 5K ₅ TaOF ₈	3.85	7.69	88.46	(L)
6K ₂ TaF ₇ + 2Ta ₂ O ₅ + 3KF $\xrightarrow{\text{expected}}$ 5K ₃ Ta ₂ O ₂ F ₉	54.55	18.18	27.27	(M)
8K₂TaF₇ + Ta₂O₅ + 4KF $\xrightarrow{\text{expected}}$ 5K₄Ta₂O₂F₁₂	61.54	7.69	30.77	(N)
4K ₂ TaF ₇ + 3Ta ₂ O ₅ + 12KF $\xrightarrow{\text{expected}}$ 5K ₄ Ta ₂ O ₃ F ₈	21.05	15.79	63.16	(O)
8K ₂ TaF ₇ + Ta ₂ O ₅ + 9KF $\xrightarrow{\text{expected}}$ 5K ₅ Ta ₂ O ₂ F ₁₃	44.44	5.56	50.00	(P)
6K ₂ TaF ₇ + 2Ta ₂ O ₅ + 13KF $\xrightarrow{\text{expected}}$ 5K ₅ Ta ₂ O ₂ F ₁₁	28.57	9.52	61.91	(Q)
11K ₂ TaF ₇ + 2Ta ₂ O ₅ + 3KF $\xrightarrow{\text{expected}}$ 5K ₅ Ta ₃ O ₂ F ₁₆	68.75	12.50	18.75	(R)
9K ₂ TaF ₇ + 3Ta ₂ O ₅ + 7KF $\xrightarrow{\text{expected}}$ 5K ₅ Ta ₃ O ₃ F ₁₄	47.37	15.79	36.84	(S)

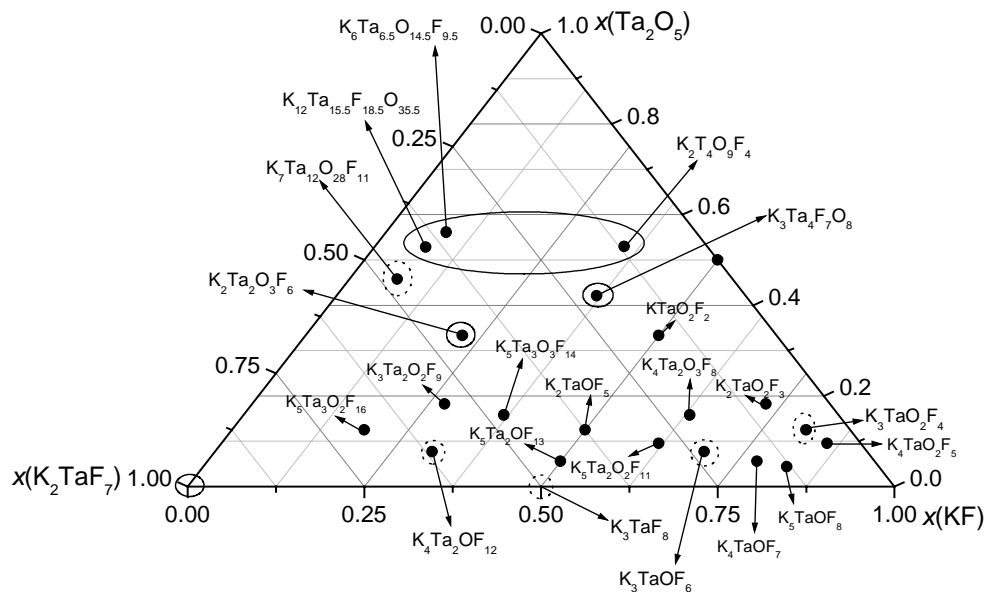


Fig. 1. Figurative points of compounds known from single crystal analysis – circled by full line; figurative points of compounds known from XRD – circled by dotted line; figurative points of compounds according to the equations from Table 2.

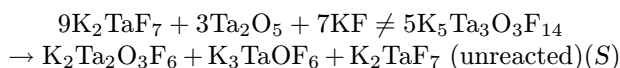
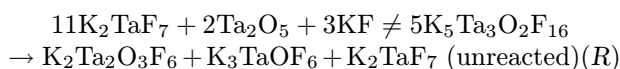
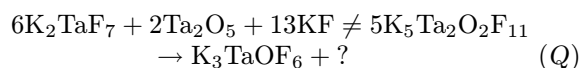
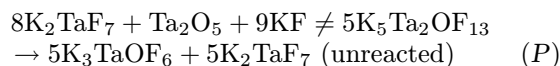
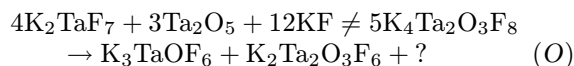
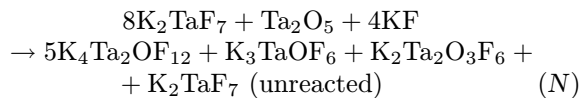
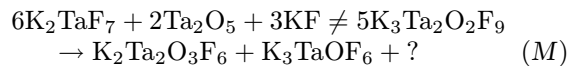
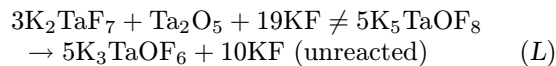
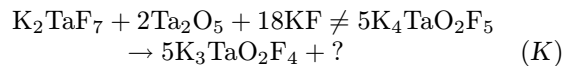
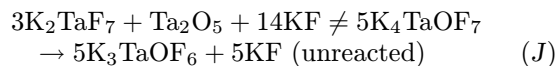
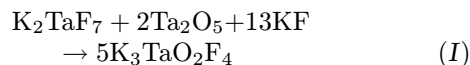
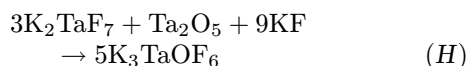
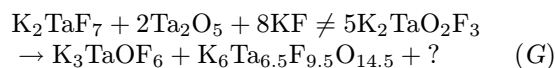
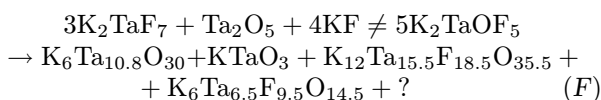
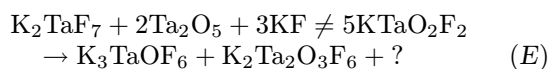
erature but neither structure nor XRD patterns are known.

It must be noted that reactions in Table 2 are only suggestions how to prepare some potassium oxofluorotantalates. Whether they exist in reality depends on the energy balance of the system under specific conditions (temperature, pressure).

The analysis of measured patterns of prepared samples was complicated by the following problems:

- i) Patterns of some single compounds are very complex.
- ii) Many reflections of two compounds overlap each other.
- iii) In the systems, more than one phase can be formed.
- iv) In the systems, products like potassium oxotantalates and potassium fluorotantalates may occur besides the potassium oxofluorotantalates.
- v) Formation of new phases in the mixtures can occur.

Finally, we have analyzed prepared samples and the following phases were observed.



As can be seen rather complicated mixtures are

formed in some cases. Thus we will summarize only unambiguous results.

Compounds K_3TaOF_6 , $K_4Ta_2OF_{12}$, and $K_3TaO_2F_4$ (bolded in Table 2) were prepared according to eqn (C). X-Ray powder pattern of $K_4Ta_2OF_{12}$ contained also other phases. Unfortunately, no single crystals suitable for X-ray analysis were found for any system.

In an attempt to prepare $KTaO_2F_2$ single crystals were obtained in an upper part of the apparatus. Determination of the cell parameters ($a = b = 19.291(1)$ Å, $c = 3.9028(5)$ Å, $\gamma = 120^\circ$) revealed the formation of $K_{12}Ta_{15.5}F_{18.5}O_{35.5}$. The bulk consists of more than one phase.

In an attempt to prepare the compound $K_2TaO_2F_3$ single crystals were obtained from the system. Measuring of the cell parameters ($a = b = 13.147(1)$ Å, $c = 3.8681(5)$ Å, $\gamma = 120^\circ$) revealed that $K_6Ta_{6.5}F_{9.5}O_{14.5}$ was formed. In the bulk the phases $K_6Ta_{6.5}F_{9.5}O_{14.5}$ and K_3TaOF_6 were identified. It means that the compound $K_2TaO_2F_3$ probably does not exist in the solid state. However, its presence is considered in liquid phase as was indicated in literature [9, 27].

Compound K_2TaOF_5 most probably does not exist in the solid state. However, its presence is considered in liquid phase as was indicated in literature [8, 9].

In the other cases more than one phase seem to be present. In some cases besides known compounds also some unidentified diffractions were observed. The number of unidentified diffractions varies from 1 to 3 and most probably they do not belong to new (expected) phase.

Heating of pure K_2TaF_7 at 1573 K provides the melt that evaporates at this temperature. Under the conditions of restricted air contact during heating single crystals were obtained. Measuring of the cell parameters revealed that $K_6Ta_{10.8}O_{30}$ was formed. Moreover, it was found that X-ray powder pattern of $K_{0.4}TaO_{2.4}F_{0.6}$ is identical to X-ray powder pattern (experimental and calculated based on structure) of $K_6Ta_{10.8}O_{30}$. It means that the compound $K_{0.4}TaO_{2.4}F_{0.6}$ previously reported [27] probably does not exist and its pattern in the PDF2 database should be deleted.

CONCLUSION

i) It is possible to write general reaction schemes for the formation of potassium oxo-fluorotantalates from three compounds. Not all possible potassium oxo-fluorotantalates can be constructed from these three compounds.

ii) According to these reaction schemes, we can suggest the reaction mixture for preparation of certain required potassium oxo-fluorotantalates. *Vice versa*, for certain mixtures we may suggest the formation of possible products.

iii) The experimental results revealed that:

a) In some cases requested compounds were formed.

b) In some cases other known compounds were identified instead of requested ones.

c) The existence of new phases cannot be excluded in spite of remarkable similarity of X-ray patterns to known ones.

iv) There is a strong need:

a) To characterize those compounds, known only from X-ray powder diffraction, by detailed structure analysis to confirm whether the suggested composition is valid.

b) For a theoretical calculation on the above system in order to predict the stability of certain ions in the melts.

The last item could be considered as a challenge to the scientific community to pay more attention to the system of oxo-fluorotantalates (similarly to oxo-fluoroniobates).

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