

A Simple Access to Pure Thorium(IV) Halides (ThCl₄, ThBr₄, and ThI₄)

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Dedicated to Professor Thomas Schleid on the Occasion of his 60th Birthday

Abstract. In this work we present a facile, lab scale synthesis for thorium tetrahalides ThX₄ (X = Cl, Br, and I). The reaction between the easily available ThO₂ and AlX₃ (X = Cl, Br, and I) and a subsequent in situ chemical vapor transport (CVT) leads to a product of high purity, which is obtained in the form of crystals or large aggregates of

crystals. Their identity and purity was evidenced by X-ray powder diffraction and IR spectroscopy. The usage of ThO₂ avoids, unlike earlier syntheses, the utilization of scarcely available thorium metal or of other reactants, such as CCl₄, which leads to impurities. Furthermore, the reaction tolerates even less pure ThO₂.

Introduction

As for uranium chemistry, also the chemistry of thorium experienced a renaissance during the past years. Since 2010 over 380 new entries of thorium compounds were added to the CSD database, even though there are only 824 entries since 1957.^[1] Also, the constant search for new nuclear reactor fuels could finally lead to thorium.^[2] In comparison to the currently mainly used nuclear fuel made out of uranium, thorium has a four times higher abundance in the earth's crust and has the potential to yield less radioactive waste.^[2] Additionally, it is much harder to use for nuclear weapons. A prototype 10 MW molten salt reactor (MSR) that uses a thorium based fuel is built by the Chinese Academy of Sciences and should be operational in 2020.^[3]

During the past two centuries, several compounds of thorium were investigated. The most frequently studied compound seems to be the acetylacetonate complex (acac) of thorium, Th(C₅H₇O₂)₄. First described by *Urbain* in 1869, many different preparation methods have been described.^[4–12a,12b] The compound has two monoclinic modifications: The α -modification is isotypic to uranium(IV) acetylacetonate and the β -modification to zirconium(IV) acetylacetonate, both with a square antiprism as coordination polyhedron for the central atom.^[13,14]

Furthermore, many complexes with β -diketones,^[15–17] alcohols,^[18] and alkoxides^[19–22] like [Th(OR)₄]_n have been described in the literature. For the tetrahalides of thorium a great number of complexes with nitrogen donors are known, mostly with a coordination number of eight for the Th atom. Important

complexes like the 8-quinolol complex, an important reagent for the gravimetric determination of thorium, were synthesized in the first half of the 20th century.^[23,24] Other examples are thorium complexes with methylamine ThCl₄(CH₅N)₄, aniline ThBr₄(C₅H₇N)₄ or even cocaine ThCl₄(C₁₇H₂₁NO₄)₂.^[25–27]

The binary halides of thorium(IV) were known since the middle of the 19th century. The first synthesis of anhydrous ThCl₄ was described by *Berzelius* in 1829 from thorium dioxide, carbon and chlorine at high temperatures.^[28] As time passed, a large variety of different syntheses had evolved, for example the reaction between thorium metal and chlorine or between thorium dioxide and disulfur dichloride.^[29,30] The crystal structure of ThCl₄ was first determined by *Mooney* from powder X-ray diffraction data and was confirmed later by *Mucker* and co-workers in 1969.^[31,32] Two polymorphs, a tetragonal high and a tetragonal low temperature form, were observed for both ThCl₄ and ThBr₄.^[33,34] The high temperature α -modification of ThCl₄ is stable above 405 °C, the one of ThBr₄ above 430 °C.

ThBr₄ was first synthesized in 1882 by *Nilson*.^[35] Many of the known preparation methods are similar to the ones known for ThCl₄, like the reaction of ThO₂ with carbon and bromine or of thorium metal directly with bromine.^[36,37] The crystal structure description by *D'Eye* reported ThBr₄ to be isotypic to ThCl₄ in space group type *I4₁/amd*.^[38]

ThI₄, also reported by *Nilson*, can be prepared directly from the elements at 300 to 500 °C.^[35,39] Alternative preparation methods are the reaction of thorium hydride with hydroiodic acid or by heating thorium metal in a mixture of iodine and hydrogen at higher temperatures.^[36] The crystal structure has been known since 1964.^[40]

The preparation methods presented here are based on our previous works, where we presented a facile synthesis of pure uranium(IV) halides (UCl₄, UBr₄, UI₄) by the reaction of UO₂ with AlX₃ (X = Cl, Br, I) using an in situ chemical vapor transport (CVT) for the purification of the product.^[41]

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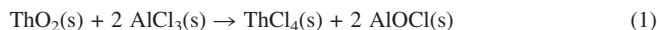
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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.201700356> or from the author.

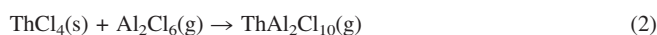
Results and Discussion

Preparation of ThCl₄

We observed that the reaction between ThO₂ and AlCl₃ leads to the formation of thorium(IV) chloride, according to Equation (1). The byproduct on the source side of the ampoule was identified as AlOCl.



With this method, the synthesis and purification time can be significantly shortened and simplified in comparison to the synthesis from the elements. ThO₂ reacted willingly with AlCl₃ at 400 °C in a flame sealed borosilicate ampoule under vacuum. A reaction time of 12 h is sufficient. Subsequently, the ampoule is placed in a single zone tube furnace with a set temperature of 500 °C at the source side and 400 °C at the sink side of the ampoule to perform an endothermal chemical transport with an excess of AlCl₃. The chemical vapor transport of ThCl₄ alone was described previously by *Schaefer* and co-workers.^[42] The formation of the gas-phase complex proceeds according to Equation (2):



The excess of AlCl₃ was chosen such that a pressure of one bar of Al₂Cl₆ was generated at the transportation temperature of 500 °C. For detailed calculations of the amount of the transport reagent and further information on the conduction of chemical vapor transport reactions, see the literature.^[42a,42b,42c]

The reaction in batch sizes between one and three grams of ThO₂ leads to several grams of pure ThCl₄ in the form of

colorless crystals or crystal aggregates with a length of up to several millimeters. A photograph of a batch can be seen in Figure 1. The syntheses and transport took three to 4 d. The isolated yields are with 95% or higher nearly quantitative. Only the colorless powder of AlOCl and the additional excess of AlCl₃ remain on the source side of the ampoule.

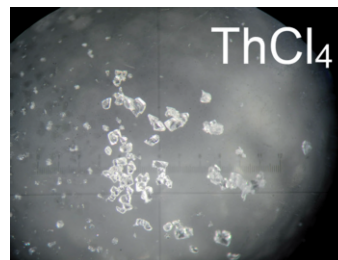


Figure 1. Photograph of ThCl₄ crystals obtained by the described method. The height of the picture corresponds to ca. 18 mm.

For batch sizes over one gram of ThO₂, the ampoule needs to be shaken several times during the reaction to break up the passivating AlOCl/ThCl₄ crust on the surface of the reaction mixture.

The powder X-ray diffraction pattern of the obtained ThCl₄ crystals is shown in Figure 2. The refined lattice parameters $a = 8.4921(1)$ and $c = 7.4835(1)$ Å of the tetragonal lattice are in good compliance with the results presented by *Mucker* and co-workers [$a = 8.486(17)$, $c = 7.465(15)$ Å, $T = 293$ K].^[43]

As expected, but also a proof for a product essentially free of moisture or hydroxides is, that the ATR IR spectrum (Figure S1, Supporting Information) shows no bands in the region

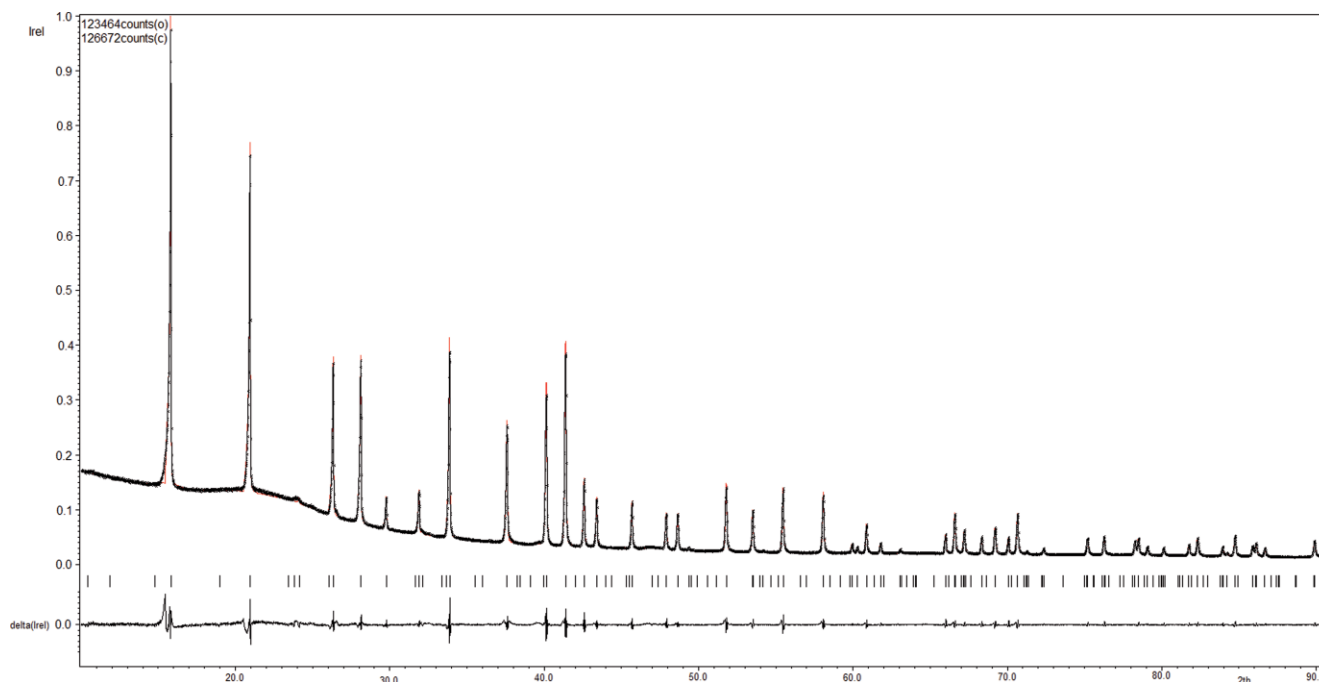


Figure 2. Powder X-ray diffraction pattern of ThCl₄ with Le Bail fitting. The calculated reflection positions are represented by lines below the observed and calculated pattern. The difference curve is plotted underneath. Profile R factors: $R_p = 2.45\%$, $wR_p = 3.78\%$, $GOF = 3.27$. The bump in the background in the area between 0 and 35° 2 θ is caused by using a nearly empty borosilicate glass capillary in order to avoid absorption.

from 4500 to 500 cm^{-1} . IR bands of ThCl_4 should be observed at 334 and 341 cm^{-1} , so there is no IR activity expected in the studied range.^[44]

As we described previously, in some cases a small quantity of a white byproduct covered the wall of the ampoule. This was identified as AlOCl stemming from the reaction of AlCl_3 with the SiO_2 of the glass ampoule.^[41,45]

Preparation of ThBr_4

The reaction between ThO_2 and AlBr_3 is similar to the reaction for the preparation of ThCl_4 . However, in order to proceed smoothly, the reaction requires a lower temperature of only 250 $^\circ\text{C}$, which is due to the higher reactivity of AlBr_3 . Therefore, the reaction temperature is distinctly lower than that used for the preparation of ThCl_4 . The temperature gradient for the endothermic chemical vapor transport is again 100 K, with 350 $^\circ\text{C}$ for the source and 250 $^\circ\text{C}$ for the sink of the ampoule. The formation of AlOBr next to the colorless crystals of ThBr_4 at the sink is also observable. A photograph of the obtained ThBr_4 crystals is shown in Figure 3.

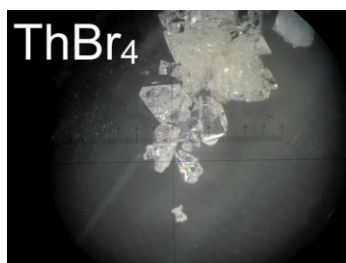


Figure 3. Photograph of ThBr_4 crystals obtained by the described method. The height of the picture corresponds to ca. 18 mm.

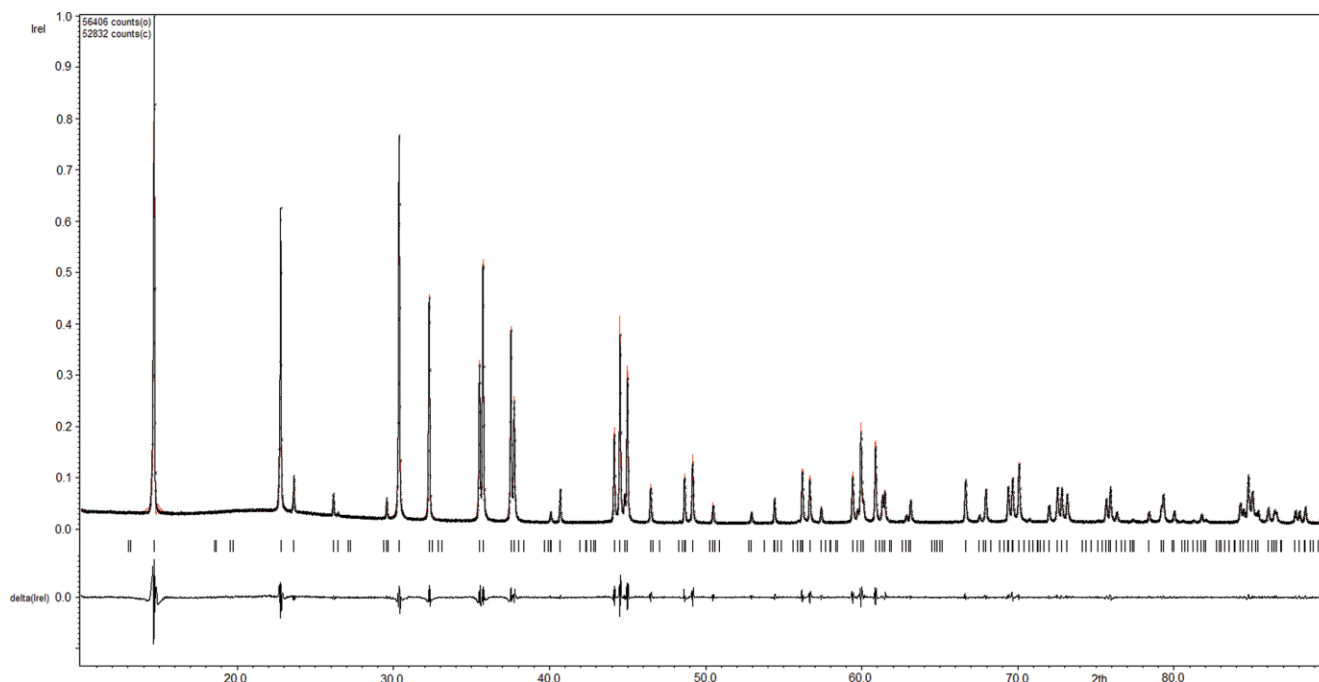


Figure 4. Powder X-ray diffraction pattern of ThBr_4 with Le Bail fitting. The calculated reflection positions are represented by lines below the observed and calculated pattern. The difference curve is plotted underneath. Profile R factors: $R_p = 4.93\%$, $wR_p = 7.18\%$, $\text{GOF} = 2.94$. The bump in the background in the area between 0 and 35 $^\circ 2\theta$ is caused by using a nearly empty borosilicate glass capillary in order to avoid absorption.

As for the reaction of UO_2 with AlBr_3 ,^[41] the reaction of AlBr_3 with the glass ampoule is clearly noticeable. Therefore, the pressure of the gas phase species Al_2Br_6 is reduced to 100 mbar which leads to a significantly higher purity of the product. The endothermic chemical vapor transport takes 3–5 d with yields of about 90% or higher. Residues of the reaction, which may still contain Th compounds, can be collected and recycled in a further batch to increase the overall yield of the preparation and minimize losses of Th.

The powder X-ray diffraction pattern of the obtained ThBr_4 crystals is shown in Figure 4. The refined lattice parameters $a = 6.7463(4)$ and $c = 13.6415(7)$ \AA of the tetragonal lattice are in good agreement with the results presented by Mason and co-workers [$a = 6.737(1)$, $c = 13.601(3)$ \AA , $T = 239$ K].^[46]

The ATR IR spectrum (Figure S2, Supporting Information) shows no bands in the region from 4500 to 500 cm^{-1} . The IR bands of ThBr_4 should be observed at ca. 45 and 230 cm^{-1} , so there is no IR activity expected in the studied range.^[47]

Preparation of ThI_4

First hints that ThI_4 could be synthesized from ThO_2 and AlI_3 at 230 $^\circ\text{C}$ were given by Chaigneau in 1957.^[48] Compared to the preparation of ThBr_4 , the pressure of the gas phase complex Al_2I_6 was reduced further, in this case to only 30 mbar in order to prevent a reaction with the borosilicate glass. The reaction was carried out at 350 $^\circ\text{C}$ and the endothermic chemical vapor transport used 450 $^\circ\text{C}$ on the source and 350 $^\circ\text{C}$ at the sink of the ampoule. The required AlI_3 was produced in situ from the elements. The canary yellow crystals of ThI_4 are shown in Figure 5.

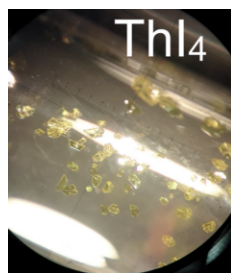
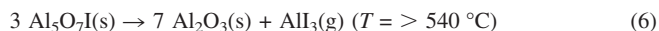
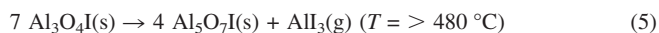
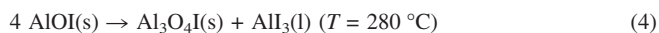
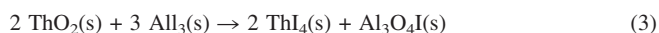


Figure 5. Photograph of ThI₄ crystals, obtained by the described synthesis method. The height of the picture corresponds to ca. 20 mm.

Because of the mentioned side reaction, the yields of the preparation method are lower than those of the chloride and bromide, only around 82 % or even lower. However, the residues of the reaction can be recycled in follow-up batches to improve the overall yield to nearly quantitative.

At the reaction temperature of 350 °C, the byproduct AlOI of the metathesis reaction between ThO₂ and AlI₃, may also convert to Al₃O₄I,^[41,49,50] however we did not observe its formation. An overview of the reactions of the aluminum oxoiodides at different temperatures and the resulting chemical equation for the reaction of ThO₂ with AlI₃ are given in Equation (3), Equation (4), Equation (5), and Equation (6).^[49]



The powder X-ray diffraction pattern of the obtained ThI₄ crystals is shown in Figure 6. The refined lattice parameters $a = 13.221(1)$, $b = 8.144(1)$ and $c = 7.832(1)$ Å, $\beta = 98.746(2)^\circ$ of the monoclinic unit cell are in good compliance with the results presented by *Zalkin* and co-workers [$a = 13.216(7)$, $b = 8.068(6)$, $c = 7.766(6)$ Å, $\beta = 98.68(5)^\circ$, T unknown].^[51]

The ATR IR spectrum (Figure S3, Supporting Information) shows no bands in the region from 4500 to 500 cm⁻¹. To the best of our knowledge, no Th–I stretching band is expected in this region, which is also shown by the measurement. Furthermore, there is no hint for common impurities like hydrolysis products.

Conclusions

The thorium(IV) halides ThX₄ ($X = \text{Cl}, \text{Br}, \text{and I}$) can be synthesized from the readily available thorium(IV) oxide and the respective aluminum(III) halide in one pot reactions by metathesis and purified by in situ chemical vapor transport. Single crystals or aggregates of crystals are obtained as the respective product, which is pure as is evidenced by powder X-ray diffraction and IR spectroscopic measurements. The method can provide several grams of ThX₄ ($X = \text{Cl}, \text{Br}, \text{I}$) per preparation. This method avoids the need for thorium metal as well as for complex apparatuses.

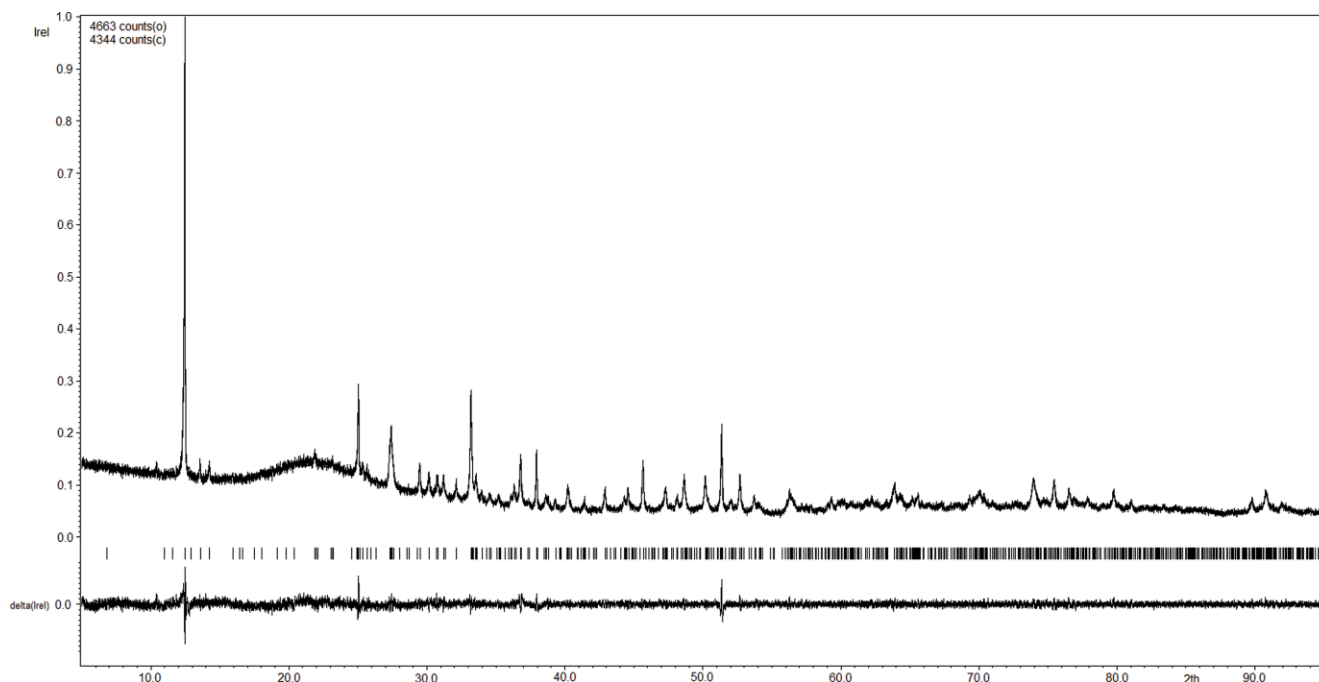


Figure 6. Powder X-ray diffraction pattern of ThI₄ with Le Bail fitting. The calculated reflection positions are represented by stokes below the observed and calculated pattern. The difference curve is plotted underneath. Profile R factors: $R_p = 4.26\%$, $wR_p = 5.44\%$, $\text{GOF} = 1.06$. The bump in the background in the area between 0 and 35° 2 θ is caused by using a nearly empty borosilicate glass capillary in order to avoid absorption. The reflection at circa 10° 2 θ is due to a tiny amount of an yet unknown impurity.

Experimental Section

All work was carried out excluding moisture and air in an atmosphere of dried and purified argon (5.0, Praxair) using high vacuum glass lines and a glovebox (MBraun).

Aluminum chloride and bromide (Merck, 98 % / Alfa Aesar, 98 %) were purified by sublimation in vacuo before use. The elemental iodine was sublimed in vacuo several times, the last time from phosphorus pentoxide. Aluminum powder (Fluka, purum > 99 %) and thorium(IV) oxide (Merck, zur Analyse) were dried in vacuo at 250 °C.

The borosilicate glass vessels were flame-dried several times under dynamic vacuum (10^{-3} mbar) before use.

For the syntheses, glass ampoules were used with a length of 16 cm, an outer diameter of 18 mm and a wall thickness of 1.5 mm as described previously.^[41] The top of the ampoule carries a NS14.5 inner ground joint for charging of the starting materials and a constriction for flame sealing. The second constriction at one-third length of the ampoule was used for the breakup of the ampoule after the reaction. The rendered 3D sketch of the ampoule is shown in Figure 7.



Figure 7. Rendered 3D sketch of the ampoule used for the synthesis of thorium(IV) halides.

The volume of the ampoules is approximately 35 mL. The pressure resistance lies between 9.5 and 11.1 bar, according to Schott Duranglas GmbH.^[18] Filling the ampoule was done inside a glove box. To protect the sink from contact with the reactants, a long glass funnel was used. Provided with a NS14.5 stopcock, the ampoule could be transferred to a Schlenk line. The content at the bottom of the ampoule was cooled with liquid nitrogen, the condensed argon removed under vacuum and the ampoule flame sealed under vacuum. Because of diffusion problems, the batch size was limited to approximately 1 g of ThO₂ in these type of ampoules. For batches with at least 3 g of ThO₂, a larger ampoule with an outer diameter of 24 mm, a wall thickness of 2 mm and a length of 16 cm was used. For the reaction and the following chemical vapor transport a standard single zone tubular furnace with a previously determined temperature gradient from the center to the end was used. The ampoule length and the calculation of the amount of transport reagent were adapted to the temperature gradient in the furnace.

Preparation of ThCl₄: Smaller Batch: An ampoule was charged with ThO₂ (1000 mg, 3.79 mmol) and AlCl₃ (1010 + 149 mg; 7.58 mmol + transport agent) and flame sealed under vacuum ($1 \cdot 10^{-3}$ mbar). The reactants were heated to 400 °C for 12 h before the transport reaction with a source temperature of 500 °C and a sink temperature of 400 °C was started. In total, 1345 mg colorless crystals of ThCl₄ (3.60 mmol, 95%) could be recovered after 3 d of transport. **Larger Batch:** An ampoule was charged with ThO₂ (3000 mg, 11.4 mmol) and AlCl₃ (3030 + 216 mg; 22.7 mmol + transport agent) and treated as described. After 4 d of transport, 4120 mg ThCl₄ (11.0 mmol, 97%) were obtained.

Preparation of ThBr₄: Smaller Batch: An ampoule was charged with ThO₂ (1000 mg, 3.79 mmol) and AlBr₃ (2020 + 38 mg; 7.58 mmol + transport agent) and flame sealed under vacuum ($1 \cdot 10^{-3}$ mbar). The

reactants were heated to 250 °C for 12 h before the transport reaction with a source temperature of 350 °C and a sink temperature of 250 °C was started. In total, 1943 mg colorless crystals of ThBr₄ (3.52 mmol, 93%) could be collected after 3 d of transport. **Larger Batch:** An ampoule was charged with ThO₂ (3000 mg, 11.4 mmol) and AlBr₃ (6060 + 64 mg; 22.7 mmol + transport agent) and treated as described. After 5 d of transport, 5782 mg ThBr₄ (10.5 mmol, 92%) were obtained.

Preparation of ThI₄: Smaller Batch: An ampoule was charged with ThO₂ (1000 mg, 3.79 mmol), Al powder (204 + 1 mg; 7.58 mmol + transport agent) and I₂ (2883 + 256 mg, 7.58 mmol + transport agent) and flame sealed under vacuum ($1 \cdot 10^{-3}$ mbar). The reactants were heated to 350 °C for 12 h before the transport reaction with a source temperature of 450 °C and a sink temperature of 350 °C was started. 2297 mg of canary yellow crystals of ThI₄ (3.11 mmol, 82%) could be extracted after 5 d of transport. **Larger Batch:** An ampoule was charged with ThO₂ (3000 mg, 11.4 mmol), Al powder (615 mg; 22.7 mmol + transport agent) and I₂ (8651 mg; 68.2 mmol + transport agent) and treated as described. After 10 d of transport, 6217 mg ThI₄ (8.41 mmol, 74%) were extracted.

The conditions for the chemical vapor transport of the thorium tetrahalides are summarized in Table 1.

Table 1. Temperatures and pressures for the studied thorium tetrahalide transport reactions.

ThX ₄ / Al ₂ X ₆	T _{source} / T _{sink} / °C	p(Al ₂ X ₆) / mbar
X = Cl	500 / 400	1000
X = Br	350 / 250	100
X = I, +I ₂ (2 bar)	450 / 350	30

Powder X-ray Diffraction: The powder X-ray diffraction patterns were recorded at room temperature with a STOE Stadi MP powder diffractometer. The diffractometer uses Cu-K_{α1} radiation, a Ge monochromator and a Mythen1K detector. The samples were powdered in a glovebox in an argon atmosphere in agate mortars and sealed into borosilicate capillaries with a diameter of 0.3 mm, which were flame-dried several times under vacuum before utilization. The evaluation of the powder X-ray diffraction patterns was carried out with the software package WinXPOW and the ICDD powder diffraction file database.^[52,53] Le Bail fitting was done with JANA 2006.^[54]

IR Spectroscopy: The IR spectra were recorded with a Bruker alpha FT-IR spectrometer using the ATR Diamond module with a resolution of 4 cm⁻¹. The spectrometer is located inside a glovebox in an argon atmosphere. The spectra were processed with the OPUS software package.^[55]

Supporting Information (see footnote on the first page of this article): The Supporting Information contains the IR spectra of the thorium halides.

Acknowledgements

F.K. thanks the Deutsche Forschungsgemeinschaft (DFG) for a Heisenberg professorship, Dr. K. Harms for measurement time, T. Chemnitz for the rendered 3D sketch of the ampoule.

Keywords: Chemical transport; Halides; Thorium

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Received: September 20, 2017

Published Online: ■

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