



Cite this: *Dalton Trans.*, 2025, **54**, 17721

## Sequential impact of niobic and tantallic acid on the synthesis of their hexa- and decametallate isopolyanions

Mark A. Rambaran 

Polyoxometalates (POMs) and their intrinsic discrete nature has enabled them to support a wide range of research spanning solution–speciation chemistry, biological/medical assays, catalytic processes and fundamental crystallography. The structure–property relationship of POMs are a consequence of their constituent metal atoms, which inevitably are formed under specific regimes – for simplicity, acidic or basic. Due to the ease of synthesis of the molybdenum and tungsten POMs, there has been relative ease in expanding their chemistry. Whereas syntheses of niobium and tantalum POMs has comparatively proven to be more challenging; albeit not often emphasised. The latter indicates the disparity in the advancement of the solution chemistry of niobium and tantalum, compared to molybdenum and tungsten. This perspective highlights the crucial points – sequentially – in developing the hexa- and decametallate POM-syntheses of niobium (polyoxoniobates) and by extension tantalum (polyoxotantalates), which benefited improving our understanding of their respective solution chemistries.

Received 29th September 2025,  
Accepted 5th November 2025

DOI: 10.1039/d5dt02333e

rsc.li/dalton

### Introduction

Niobium (Nb) and tantalum (Ta) are refractory metals and inherently exhibit excellent resistance to heating, abrasion and corrosion. These properties are desirable for applications in surface coatings, mining and metal fabrication. Niobium in particular is important in the fabrication of high-strength low-alloy steel.<sup>1</sup> Tantalum tends to be more expensive than niobium and is predominantly used in manufacturing of electrolytic capacitors.<sup>2</sup> Notably the corrosion resistance exhibited by niobium and tantalum is underpinned by the presence of a thin layer of oxide at the surface – *i.e.* Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub>, respectively. Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> possess charge intercalation and dielectric properties, respectively.<sup>2,3</sup> This corresponds to their use in electrochemical energy storage (*e.g.* Li-ion batteries),<sup>3</sup> and electrical components as capacitors,<sup>2</sup> respectively. Furthermore, the inertness and corrosion resistance of niobium and tantalum makes them biocompatible. This is attractive for developing orthopaedic implants.<sup>4</sup>

By no means is this an exhaustive list of applications derived from niobium and tantalum. Rather, it is to highlight the different facets of society which benefit from applications attributable to these materials. Thus, understanding the solution chemistry of niobium and tantalum oxides is important

for expanding the application of these materials, as well as improving recycling efforts to foster sustainable manufacturing. Previous reviews by Nyman,<sup>5</sup> Zhao,<sup>6</sup> and Yang<sup>7</sup> elucidate advancements in the synthesis of polyoxoniobates and polyoxotantalates, and the relevance of this to their respective applications, especially catalysis. In this perspective, however, the benefits derived from using niobic and tantallic acids to synthesise polyoxoniobates and polyoxotantalates, respectively, is succinctly expressed to accentuate the impact it has had in achieving hexa- and decametallate polyoxometalate species of niobium and tantalum.

### Polyoxometalates (POMs)

POMs have garnered significant interest well over a century owing to their structural and solution chemistry. They include the polyoxovanadates (POV), polyoxoniobates (PONb), polyoxotantalates (POTa), polyoxomolybdates (POMo) and polyoxotungstates (POW). A common aphorism, one could even say “*adage*”, within the field of polyoxometalates (POMs), is to define them as “discrete metal oxoanion clusters of the group V (V, Nb and Ta) and VI (Mo and W) metals, in their highest oxidation states”.<sup>8</sup> Notably, although Cr is the lightest congener of the group VI metals, it is generally not considered to form polyoxometalate species. This is because Cr<sup>6+</sup> has a tendency to form a tetrahedral four-coordination oxide, rather than the metal octahedron associated with discrete metal oxoanion clusters.<sup>9</sup>

Centre for Analysis and Synthesis and NanoLund, Lund University, 22100 Lund, Sweden. E-mail: mark.rambaran@chem.lu.se



As explained by Pope and Müller,<sup>10</sup> the structures of POMs follow two basic principles: (1) each metal atom occupies a metal polyhedron ( $\text{MO}_x$ ; predominantly octahedron or square pyramid) where metals are displaced towards the polyhedral vertices, and (2) POMs generally do not exhibit structures which contain three or more  $\text{MO}_6$  octahedron with free vertices – a consequence of the Lipscomb restriction.<sup>11</sup> For a general historical account of POMs – *which is beyond the scope of this perspective* – see the review by Pope and Müller.<sup>10</sup>

Historically there has been relative ease in synthesising POV, POMo and POW, comparatively to the polyoxoniobates and –tantalates. This is largely influenced by the aqueous solubility (*under acidic conditions*) and commercial availability of the precursors for synthesising POV, POMo and POW.<sup>12</sup> For example, decavanadate can be made through acidifying stock solutions of ammonium metavanadate.<sup>13</sup>

Phosphomolybdic acid ( $\text{H}_3[\text{Mo}_{12}\text{PO}_{40}]$ ), a heteropolyacid of molybdenum, can be made from dissolution of ammonium heptamolybdate or molybdenum trioxide in phosphoric acid, with heating, followed by acidification with HCl.<sup>14</sup> Similarly, phosphotungstic acid ( $\text{H}_3[\text{W}_{12}\text{PO}_{40}]$ ) is made by heating sodium tungstate dihydrate and disodium hydrogen phosphate in water, followed by acidification with HCl.<sup>15</sup> Both phosphomolybdic and phosphotungstic acids require acidic conditions for the polyoxometalates to remain intact. This is unlike the case for the PONb and POTa, which precipitate as hydrous  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$ , respectively, under acidic conditions.<sup>16,17</sup>

The relative ease of using aqueous synthetic methods to make the POV, POMo and POW from very early on has benefited the expansion of the fields related to these POMs. Conversely, there was no prior ease in the synthesis of PONb or POTa. There is no inorganic salt of niobium(v) or tantalum(v), or water-soluble metal oxide that facilitates aqueous synthesis of PONb and POTa, respectively. Despite niobium and tantalum being discovered over two centuries ago, their respective solution chemistry is well known relative to the formation of fluoroniobates and fluorotantalates. The aforementioned is consistent with their intrinsic fluoride chemistry enabling extraction and separation of niobium and tantalum from mineral ores.<sup>18</sup> This was beneficial in developing the industrial production of metallic niobium and tantalum.

However, while there are alternative organometallic reagents, such as niobium chloride and niobium pentaethoxide, they are however highly susceptible to hydrolysis – spurring formation of hydrous  $\text{Nb}_2\text{O}_5$ . This reiterates the issue of insolubility in acidic medium.<sup>19</sup> There is ammonium niobium oxalate, but this also yields hydrous  $\text{Nb}_2\text{O}_5$  with removal of the oxalate anion.<sup>20</sup> A similar result occurs – *i.e.* formation of hydrous  $\text{Ta}_2\text{O}_5$  – for the analogous tantalum chloride, ethoxide and oxalate. With the current state-of-the-art, access to water soluble PONb and POTa is achieved through synthesis *via* hydrous (niobic acid) or anhydrous  $\text{Nb}_2\text{O}_5$ , and hydrous  $\text{Ta}_2\text{O}_5$  (tantalac acid), respectively, in basic medium – albeit this was not always the case.<sup>16</sup> Of course there are also other heteropo-

lyanions of niobium and tantalum, such as the Keggin and Anderson derivatives,<sup>5</sup> however these will not be discussed in detail since the hexametalate and decametalate POM structures are prioritised in this perspective for the period 2002–2022.

The isopolyanions of niobium of interest herein are the decaniobate ion ( $[\text{Nb}_{10}\text{O}_{28}]^{6-}$ , **Nb<sub>10</sub>**), and the hexaniobate ion ( $[\text{Nb}_6\text{O}_{19}]^{8-}$ , **Nb<sub>6</sub>**). Although both species can be made from the same niobium precursor (niobic acid), each exhibits a distinct solution chemistry, albeit they differ by the number of their constituent metal atoms. For example, **Nb<sub>10</sub>** is stable near at neutral pH, while the hexaniobate ion **Nb<sub>6</sub>** predominates at  $\text{pH} > 9$ .<sup>16,17</sup> Furthermore, **Nb<sub>6</sub>** is accessible from both hydrous  $\text{Nb}_2\text{O}_5$  and anhydrous  $\text{Nb}_2\text{O}_5$ , *via* a one-pot synthesis which commences at  $\text{pH} > 13$ ; whereas **Nb<sub>10</sub>** is not directly accessible from anhydrous  $\text{Nb}_2\text{O}_5$ .<sup>16</sup> The pH stability range exhibited by these PONb ( $7 > \text{pH} > 14$ ) is a distinctive feature, as neither the POMo or POW are typically stable in this pH range. Likewise, formation of the hexatantalate species ( $[\text{Ta}_6\text{O}_{19}]^{8-}$ , **Ta<sub>6</sub>**), which is isostructural to **Nb<sub>6</sub>**, requires  $\text{pH} \geq 12$  to promote dissolution of tantalac acid to yield this species.<sup>16</sup> Hence, the PONb and POTa are the only species that remain intact under basic pH conditions. Aside from the base stability of the PONb and POTa, their aqueous solubility is also influenced by the counter ions present, especially in the case of alkali cations.<sup>21–24</sup> Furthermore, there is a lack of redox chemistry for the PONb and POTa, whereas the POMo and POW are active in this regard.<sup>5</sup>

The POV, on the other hand, are soluble under basic conditions; however, depending on pH and ionic strength, there is speciation between different oligomeric POV species. These include the monomeric ( $[\text{VO}_4]^{3-}$ , at high pH), dimeric ( $[\text{V}_2\text{O}_7]^{4-}$ ), tetrameric ( $[\text{V}_4\text{O}_{12}]^{4-}$ ), pentameric ( $[\text{V}_5\text{O}_{15}]^{5-}$ ) vanadates in aqueous vanadium(v) solutions.<sup>13,25</sup> The decavanadate ion ( $[\text{V}_{10}\text{O}_{28}]^{6-}$ , **V<sub>10</sub>**) is another species consisting of ten  $\text{VO}_6$  octahedra connected to form a decametalate structure like decaniobate. The **V<sub>10</sub>** species predominates at  $\text{pH} 3.0\text{--}5.8$ , however above this pH it dissociates to form other oligomeric species.<sup>13</sup>

### Synthesis of polyoxoniobates and -tantalates before hydrous oxides

Interestingly, element 41 (Nb), was initially called “Columbium (Cb)” up until arbitration by the International Union of Pure and Applied Chemistry (IUPAC) in 1950, where the name “Niobium” and symbol Nb were officially adopted.<sup>26</sup> Therefore, prior to 1950, there would have been studies – predominantly in North America – which would have referenced Columbium or coulombic oxide as the species of interest in research.<sup>27</sup> For example, the alkali-hexaniobate species  $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$ , was isolated as in 1908 by Balke and Smith, *via* a molten salt reaction (*discussed in more detail below*).<sup>28</sup> Despite the nomenclature used in their work being related to columbium, it sufficiently contributed to future work focused on unearthing the solution chemistry of niobium;<sup>29</sup> especially as it related to polyoxometalates.



One of the earlier methods, from 1941, to synthesise polyoxoniobates and -tantallates relied on fusing anhydrous  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$ , with molten alkali carbonate or hydroxide salts to dissolve the metal oxide.<sup>30</sup> This method, akin to prior work by Balke and Smith,<sup>28</sup> can only yield the “Lindqvist type” hexametalate ion ( $[\text{M}_6\text{O}_{19}]^{8-}$ ,  $\text{M} = \text{Nb}$  or  $\text{Ta}$ ); which is named after Ingvar Lindqvist as homage to his work with the POMo from 1953.<sup>31</sup> The Lindqvist ion is the POM species obtainable from niobium ( $\text{Nb}_6$ ) and tantalum ( $\text{Ta}_6$ ) in aqueous solution at  $\text{pH} > 9$ . The structure of the Lindqvist ion (Fig. 1A) consists of six edge-sharing  $\text{MO}_6$  octahedra connected to form twelve  $\text{M}-\text{O}-\text{M}$  bridges, called  $\mu_2\text{-O}$  groups. Each metal centre of the  $\text{MO}_6$  octahedra is bonded to a central oxygen atom ( $\mu_6\text{-O}$ ), and each  $\text{MO}_6$  octahedra is also capped with a terminal  $\text{M}=\text{O}$  group ( $\eta = \text{O}$ ); *i.e.* a total of six  $\eta = \text{O}$  groups.

In 1965 it was determined from work by Guerchai and Spinner on ammonium niobates, that the ammonium hexaniobate species  $(\text{NH}_4)_7[\text{HNb}_6\text{O}_{19}]$  was accessible.<sup>32</sup> By 1977, the other isopolyoxoniobate ( $\text{Nb}_{10}$ ) was synthesised through the slow hydrolysis of niobium pentaethoxide, in the presence of tetramethylammonium hydroxide (TMAOH), by Graeber and Morosin.<sup>19</sup> This reaction was essentially dependent on the dissolution of  $\text{Nb}_2\text{O}_5$  in TMAOH, as the moisture sensitivity of niobium pentaethoxide inevitably results in the formation of hydrous  $\text{Nb}_2\text{O}_5$ , *i.e.* niobic acid. The use of the poorly aqueous soluble  $\text{Nb}_2\text{O}_5$  was never circumvented. However, hydrolysis of niobium pentaethoxide renders the formation of niobic acid ( $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ),<sup>19</sup> which turned out to be suitable precursor for future PONb syntheses. Many years later, this approach to the hydrolysis of organometallic precursors – such as  $\text{TaCl}_5$  – would be beneficial in developing peroxide ligation for the synthesis of polyoxotantalates.<sup>33,34</sup> For example, Anderson *et al.*<sup>34</sup> used  $\text{TaCl}_5$  as the Ta precursor for synthesis of alkali peroxy-tantalates ( $\text{Rb}_3\text{Ta}(\text{O}_2)_4$  and  $\text{K}_3\text{Ta}(\text{O}_2)_4$ ). These products could thereafter undergo alkali dissolution to spur formation of hydrous  $\text{Ta}_2\text{O}_5$ , which enabled synthesis of  $[\text{Ta}_6\text{O}_{19}]^{8-}$ . Notably, Anderson *et al.*<sup>34</sup> determined the latter process could

be improved *via*  $[\text{VO}_4]^{3-}$  catalysed peroxide decomposition, to spur faster formation of  $\text{Ta}_2\text{O}_5$ . What is noteworthy is that this method was devised out of a need to overcome the limited commercial availability of hydrous  $\text{Ta}_2\text{O}_5$ ,<sup>34</sup> and so underscores the significance of hydrous  $\text{Ta}_2\text{O}_5$  in the synthesis of polyoxotantalates.

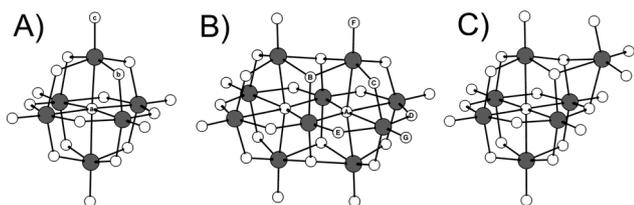
Notably, there are several forms of  $\text{Nb}_2\text{O}_5$ , which include crystalline (orthorhombic and monoclinic) and amorphous (niobic acid) phases.<sup>35</sup> Neither of these forms of  $\text{Nb}_2\text{O}_5$  are readily soluble in water. However, the dissolution of niobic/tantallic acid in basic medium, is crucial for future development of polyoxoniobate and -tantallate syntheses. Notwithstanding this, the moisture sensitivity of the niobium pentaethoxide in this reaction gave poor reproducibility overall in this method, and the initial  $\text{Nb}_{10}$  synthesis wasn't reproduced in the literature until nineteen years later – 1996.<sup>36</sup>

The decaniobate ion (Fig. 1B) mentioned previously consists of ten  $\text{NbO}_6$  octahedra connected in such a way that there are seven types of structurally unique oxygens. There are three sets of  $\mu_2\text{-O}$  groups (D is a set of two, E is a set of four and C a set of eight), two sets of four  $\eta = \text{O}$  groups (G and F), two  $\mu_6\text{-O}$  groups, and one set of four oxygen atoms connected to three metal centres ( $\mu_3\text{-O}$ , site B). Due to the  $\mu_2\text{-O}$ ,  $\mu_3\text{-O}$ ,  $\eta = \text{O}$  and  $\mu_6\text{-O}$  all being structurally distinct sites in the POM structure, they can be distinguished through their NMR signals, after isotopic substitution with  $^{17}\text{O}$  nuclei, in  $^{17}\text{O}$  NMR spectroscopy (*vide infra*).<sup>17,37–41</sup>

### Impact of niobic acid on the aqueous synthesis of polyoxoniobates

The crucial change in polyoxoniobate synthesis occurred in 2002 – twenty five years after 1977 – when niobic acid was used by Nyman *et al.*<sup>42</sup> as the precursor in the synthesis of the Keggin type heteropolyniobates. Afterwards, Nyman *et al.*<sup>43</sup> reacted niobic acid with titanium isopropoxide under hydrothermal conditions, in the presence of aqueous  $\text{NaOH}$ , to yield the titanoniobate isopolyanion  $[\text{Ti}_2\text{Nb}_8\text{O}_{28}]^{8-}$  ( $\text{Ti}_2\text{Nb}_8$ ).<sup>43</sup> Next came the first one-pot, alkali-free synthesis of  $\text{Nb}_{10}$ , through use of TMAOH as a base, to yield the tetramethyl ammonium (TMA) salt  $[\text{N}(\text{CH}_3)_4]_6[\text{Nb}_{10}\text{O}_{28}]^{6-}$ .<sup>44</sup> Thereafter came progressive expansion in the field of PONb and POTa chemistry. This included the synthesis of other titanoniobate isopolyanions, and heterometal substituted PONb and POTa.<sup>45–52</sup> A distinctive feature – rather an advantage – of the TMA-PONb and TMA-POTa salts compared to their alkali counterparts, is the remarkable solubility exhibited by the TMA salts. They are highly soluble in water (*ca.* 1 gram per millilitre); also soluble in methanol and ethanol, but not acetone, isopropanol nor acetonitrile.<sup>44</sup>

With the newfound capability to synthesise PONb *via* niobic acid with high reproducibility came the studies of the solution chemistry of niobium(v), which were previously lacking.  $^{17}\text{O}$  NMR spectroscopic studies were an invaluable asset to elucidating niobium(v) solution chemistry.<sup>53,54</sup> Notably, the POMo, POW and POV are easily detectable due to the natural abundance and sensitivity of the  $^{95}\text{Mo}$  and  $^{97}\text{Mo}$ ,



**Fig. 1** (A) The Lindqvist (hexametalate) ion hexaniobate ( $[\text{Nb}_6\text{O}_{19}]^{8-}$ ,  $\text{Nb}_6$ ), with structurally unique oxygens labelled a:  $\mu_6\text{-O}$ , b:  $\mu_2\text{-O}$  and c:  $\eta = \text{O}$ . (B) The decametalate ion, decaniobate ( $[\text{Nb}_{10}\text{O}_{28}]^{6-}$ ,  $\text{Nb}_{10}$ ) with each structurally unique oxygen labelled. A:  $\mu_6\text{-O}$ ; B:  $\mu_3\text{-O}$ ; C–E:  $\mu_2\text{-O}$ ; F–G:  $\eta = \text{O}$ . (C) The heptaniobate ion ( $[\text{Nb}_7\text{O}_{22}]^{7-}$ ,  $\text{Nb}_7$ ) which forms as an intermediate in the dissociation of  $\text{Nb}_{10}$  to  $\text{Nb}_6$ . White spheres represent oxygen and grey niobium. (A) and (B) Adapted from ref. 16 with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim,<sup>16</sup> copyright 2019. (C) Adapted from ref. 17 with permission from WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim,<sup>17</sup> copyright 2008. Structures were drawn using Chemcraft, Version 1.8, build 682.



$^{183}\text{W}$  and  $^{51}\text{V}$  NMR nuclei, respectively.<sup>55</sup> This has been beneficial especially to elucidating the speciation and structure of the POW,<sup>8,55</sup> and POV.<sup>25</sup> However, an NMR active nuclei of Nb or Ta that is present in high abundance and sensitivity to facilitate NMR experiments is unavailable. The  $^{93}\text{Nb}$  and  $^{181}\text{Ta}$  nuclei are quadrupolar which make them less sensitive, while exhibiting broad NMR signals that cover a large portion of the spectra window.<sup>55</sup> The  $^{93}\text{Nb}$  and  $^{181}\text{Ta}$  nuclei are also the only stable isotopes of niobium and tantalum, respectively, which adds further challenges. For example, this is manifested through the difficulty in determining the charge of the POM species, based on the shape of the signal envelope, for Nb and Ta POMs through electrospray ionisation mass spectrometry (ESI-MS).<sup>56</sup> Comparatively, the larger number of naturally occurring isotopes of Mo and W do not incur this challenge.

The oxygen-exchange between the  $^{17}\text{O}$  and  $^{16}\text{O}$  nuclei, of  $\text{H}_2^{17}\text{O}$  and  $\text{H}_2^{16}\text{O}$ , respectively, in water occurs on timescales that are sufficiently long enough for detailed  $^{17}\text{O}$  NMR studies.<sup>39,40,57</sup> This effectively mitigated the lack of an NMR active nucleus for probing the *in situ* solution chemistry of both niobium(v) and tantalum(v). Furthermore, the fact that the PONb and POTa clusters all possess structurally distinct oxygens groups ( $\mu_2\text{-O}$ ,  $\mu_3\text{-O}$ ,  $\mu_6\text{-O}$  and  $\eta = \text{O}$ ) allows the discernment of their respective  $^{17}\text{O}$  NMR signals for structure elucidation.

The *in situ* monitoring of the PONb and POTa solution chemistry is pertinent to improving the synthesis of these POMs, since they are conventionally reliant on hydrothermal methods that obscure real time monitoring of the reaction. Understanding the dissolution of these oxides, on the molecular scale, is beneficial for determining the impact of geochemical processes related to the dissolution of these oxides

on the macro scale.<sup>58</sup> Techniques such as  $^{17}\text{O}$  NMR spectroscopy and Raman spectroscopy, which take advantage of the POM's structurally distinct metal-oxo groups, are therefore useful in expanding our knowledge of the solution chemistry of niobium(v) and tantalum(v).<sup>13,16,35</sup> *In situ* TEM has even been demonstrated as beneficial in using PONb to monitor the real-time formation of heterometal-niobates, which further accentuates the benefits in understanding crystallisation of solid-state niobium oxides.<sup>59</sup>

Raman spectroscopy is particularly useful, because it is non-destructive, quick and provides a wealth of structural information about the POMs. More so, the PONb and POTa are colourless in aqueous solution and their relevant metal-oxygen Raman shifts do not coincide with that of water, which makes them excellent candidates for aqueous *in situ* Raman studies. This was advantageous in determining the "activation pH" of anhydrous  $\text{Nb}_2\text{O}_5$ , anhydrous  $\text{Ta}_2\text{O}_5$ , niobic, and tantallic acid. Furthermore, this activation pH made it possible to discern the limiting pH for forming specific PONb and POTa in a one-pot process, depending on the precursor used.<sup>16</sup>

Along with the synthesis of  $\text{Ta}_6$  in non-aqueous medium,<sup>60</sup> other synthetic advancements in tantalum(v) chemistry include syntheses of the decatantalate ion ( $[\text{Ta}_{10}\text{O}_{28}]^{6-}$ ,  $\text{Ta}_{10}$ ),<sup>61</sup> and a hexatantalate tetramer.<sup>62</sup> The use of tetrabutylammonium hydroxide (TBAOH) facilitated the non-aqueous synthesis in these methods. However, an aqueous one-pot synthesis to the  $\text{Ta}_{10}$  ion is yet to be achieved – despite separate attempts using tantalum pentaethoxide,<sup>37</sup> and tantallic acid.<sup>16</sup> Notably, the inability to make the  $\text{Ta}_{10}$  ion directly *via* a one-pot synthesis, in aqueous medium, was determined to be a consequence of the 'activation pH'.<sup>16</sup> The activation pH dictates that the molecules accessible from a specific metal oxide,

**Table 1** Notable syntheses in advancing polyoxoniobate and polyoxotantalate chemistry

Year	Activity	Author(s)	Product(s)	Outcome
1908	Molten salt reaction	Balke and Smith <sup>28</sup>	$\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$	Isolated alkali PONb
1965	Synthesis of ammonium niobates	Guerchai and Spinner <sup>32</sup>	$(\text{NH}_4)_7(\text{HNB}_6\text{O}_{19})$ ( $\text{Nb}_6$ )	Alkali-free PONb accessible
1977	Slow base hydrolysis	Graeber and Morosin <sup>19</sup>	$[\text{N}(\text{CH}_3)_4]_6[\text{Nb}_{10}\text{O}_{28}]$ ( $\text{Nb}_{10}$ )	Alkali-free $\text{Nb}_{10}$ isolated
1996	Slow base hydrolysis	Lee and Crayston <sup>36</sup>	$[\text{N}(\text{CH}_3)_4]_6[\text{Nb}_{10}\text{O}_{28}]$ ( $\text{Nb}_{10}$ )	Reproducible $\text{Nb}_{10}$ synthesis
2003	Hydrothermal synthesis with niobic acid	Nyman <i>et al.</i> <sup>43</sup>	$\text{Na}_8[\text{Ti}_2\text{Nb}_8\text{O}_{28}]$ ( $\text{Ti}_2\text{Nb}_8$ )	Base-soluble precursor for reproducible PONb synthesis
2006	Non-aqueous synthesis with hexaniobate	Maekawa <i>et al.</i> <sup>63</sup>	$[\text{TBA}]_8[\text{Nb}_{20}\text{O}_{54}]$ ( $\text{Nb}_{20}$ )	Icosoniobate synthesis
2009	One-pot alkali-free PONb synthesis	Ohlin <i>et al.</i> <sup>44,45</sup>	$[\text{N}(\text{CH}_3)_4]_7[\text{TiNb}_9\text{O}_{28}]$ ( $\text{Nb}_6$ ), ( $\text{Nb}_{10}$ ), ( $\text{TiNb}_9$ )	Reproducible PONb synthesis
2011	Non-aqueous synthesis	Matsumoto <i>et al.</i> <sup>60</sup>	$[\text{TBA}]_6[\text{H}_2\text{Ta}_6\text{O}_{19}]$ ( $\text{Ta}_6$ )	Hexatantalate synthesis
2013	Non-aqueous synthesis	Matsumoto <i>et al.</i> <sup>61</sup>	$[\text{TBA}]_6[\text{Ta}_{10}\text{O}_{28}]$ ( $\text{Ta}_{10}$ )	Decatantalate synthesis
2019	Microwave synthesis	Rambaran <i>et al.</i> <sup>16</sup>	( $\text{Nb}_6$ ), ( $\text{Nb}_{10}$ ), ( $\text{Ta}_6$ )	Fast, high yield PONb and POTa syntheses



is limited to species stable at or above the activation pH of the oxide in a one-pot synthesis.<sup>16</sup> The determination of this activation pH, was also made possible through availability of niobic and tantalic acid, which facilitated *in situ* Raman studies for monitoring POM formation.<sup>16</sup>

Non-aqueous synthesis of isopolyoxoniobates – achieved *via* acidification of Nb<sub>10</sub> – resulted in the formation of the icosaniobate ([Nb<sub>20</sub>O<sub>54</sub>]<sup>8-</sup>, Nb<sub>20</sub>) ion,<sup>63</sup> which was also formed through dimerization of two Nb<sub>10</sub> species.<sup>64</sup> Similarly, an aqueous one-pot synthesis of Nb<sub>20</sub> from niobic acid has not been achieved, which is a limitation attributable to the activation pH of niobic acid.<sup>16</sup> Finally, of the aforementioned syntheses, a chronological listing of noteworthy synthetic advancements in making PONb and POTa species is given in Table 1.

## Exploring the solution chemistry of niobium(v) *via* the polyoxoniobates

Notable examples of investigations using <sup>17</sup>O NMR spectroscopy to probe the solution chemistry of polyoxoniobates includes determining the isotope-exchange dynamics of the Nb<sub>10</sub>,<sup>17</sup> monotitanoniobate (TiNb<sub>9</sub>),<sup>40</sup> and dititanoniobate (Ti<sub>2</sub>Nb<sub>8</sub>) ions.<sup>41</sup> Studies of the formation and reactivity of peroxopolyoxoniobate species – from the peroxidation of Nb<sub>10</sub> and Nb<sub>6</sub> – was also possible through <sup>17</sup>O NMR spectroscopy.<sup>65</sup> Considering H<sub>2</sub>O<sub>2</sub> is a by-product associated with photocatalysis,<sup>66</sup> and the sequestration of radionuclides from waste,<sup>67</sup> of which niobium oxides are used,<sup>67–70</sup> it is relevant to understand the reactivity of PONb and H<sub>2</sub>O<sub>2</sub>. Furthermore, there are similar studies of the Nb<sub>6</sub> and Ta<sub>6</sub> ions that are reliant on <sup>17</sup>O NMR spectroscopy, however these were in the presence of alkali cations.<sup>21,39,57</sup>

The Nb<sub>10</sub> cluster is stable at pH 5–7, while at pH ≥ 7.5 dissociation to the Nb<sub>6</sub> cluster commences.<sup>17</sup> Moreover, this base enhanced dissociation becomes rapid at pH > 9.3, through the formation of the heptaniobate ([Nb<sub>7</sub>O<sub>22</sub>]<sup>9-</sup>, Nb<sub>7</sub>) intermediate and this was confirmed through monitoring the isotopic oxygen-exchange *via* <sup>17</sup>O NMR.<sup>17,38</sup> The site-specific substitution of a single central Nb(v) atom with a Ti(IV) atom in the TiNb<sub>9</sub> cluster extends the stability range of the decametallate to pH 6.5–12.<sup>40,71</sup> Substitution of another central Nb(v) atom with a Ti(IV) atom, to form the Ti<sub>2</sub>Nb<sub>8</sub> ion offers enhanced stability to base dissociation, as the cluster remains intact at even at pH 12.5.<sup>41</sup> Considering this, it was envisaged that heteroatom substitution within the Nb<sub>10</sub> cluster, may similarly influence structural changes in the formation of solid-state niobates.

For example, it was determined by Rambaran *et al.*<sup>35</sup> that different titanium–niobium oxides Ti<sub>2</sub>Nb<sub>10</sub>O<sub>29</sub> and TiNb<sub>2</sub>O<sub>7</sub>, were accessible *via* the TiNb<sub>9</sub> and Ti<sub>2</sub>Nb<sub>8</sub> polyoxoniobates, respectively. The *in situ* monitoring of the solution chemistry of the titanoniobate clusters was similarly possible through studying the isotopic oxygen-exchange *via* <sup>17</sup>O NMR spectroscopy. It was also possible to determine that borate significantly enhances the oxygen-exchange of PONb (Nb<sub>6</sub>, Nb<sub>10</sub> and

Ti<sub>2</sub>Nb<sub>8</sub>), a significant finding since borate is often used a pH buffer due to its low cost and the assumption that it is inert.<sup>72</sup>

Understanding the dissolution of Nb<sub>2</sub>O<sub>5</sub> is dependent on knowing which PONb species is/are dominant at a particular pH and their stability, as this is relevant to geochemical processes and the formation of niobate minerals in the environment.<sup>73</sup> Consider the minerals Peterandresanite,<sup>74</sup> hanesmar-kite,<sup>75</sup> and melcherite,<sup>76</sup> all contain the Nb<sub>6</sub> species. Since these minerals were formed at low temperatures (≤350 °C), it suggests Nb<sub>6</sub> is the transport medium for aqueous niobium in the environment, which contradicts the assumption of it being immobile.<sup>73</sup> The significance of this comes full-circle when the activation pH of niobic acid (pH ≥ 6.9) and anhydrous Nb<sub>2</sub>O<sub>5</sub> (pH ≥ 12) is considered, alongside the pH stability of the Nb<sub>10</sub>.

Dissolution of niobic acid – to yield both Nb<sub>6</sub> and Nb<sub>10</sub> – and anhydrous Nb<sub>2</sub>O<sub>5</sub> (only Nb<sub>6</sub> formed) has occurred at 180 °C during hydrothermal syntheses.<sup>16</sup> Though the temperatures used in these syntheses are *ca.* 50% lower than 350 °C, dissolution commenced at pH > 13 and continued with an accompanying decrease in pH. More so, the pH decreased down to the respective activation pH, with no further diminution.<sup>16</sup> The formation of Nb<sub>6</sub> from these syntheses was detectable with Raman spectroscopy at 10 ≤ pH ≤ 13, and is therefore consistent with Nb<sub>6</sub> only being found in minerals from alkaline rocks.<sup>73</sup>

For the Nb<sub>10</sub> species, which is normally stable at neutral pH, as it rapidly dissociates to the Nb<sub>6</sub> at pH ≥ 9.3, it forms a tetranioabate fragment that forms higher oligomers like the heptaniobate ion (Fig. 1C).<sup>17</sup> The heptaniobate ion, initially discovered by Niu *et al.*,<sup>77</sup> has been determined to assemble into the larger [Nb<sub>24</sub>O<sub>72</sub>]<sup>24-</sup> cluster in the presence of alkali cations,<sup>24,78</sup> which is consistent with it being a building block for the assembly of larger PONb.<sup>79</sup>

Previous studies have independently shown that there is both a pH dependence, and an influence of alkali counter ions, on the formation of the heptaniobate species, occurring *via* the dissociation of Nb<sub>10</sub> to Nb<sub>6</sub>.<sup>17,24,78</sup> On the molecular scale, the significance of these findings are relevant to elucidating the processes involved in the assembly of large PONb clusters, such as the [HNb<sub>27</sub>O<sub>76</sub>]<sup>16-</sup>, [H<sub>10</sub>Nb<sub>31</sub>O<sub>93</sub>(CO<sub>3</sub>)]<sup>23-</sup>, [Nb<sub>24</sub>O<sub>72</sub>]<sup>24-</sup> and [Nb<sub>32</sub>O<sub>96</sub>]<sup>32-</sup> clusters.<sup>79,80</sup> On the scale of geochemical processes this means that there is a duality, relative to pH dependence and the presence of alkali counter ions – rather than a mere coincidence – in the formation of Nb<sub>6</sub> containing minerals which are only found in alkaline rocks.<sup>73–75,81</sup>

### Applications of polyoxoniobates

The ability to fabricate solid-state Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> thin films or functional surfaces through aqueous deposition of POM solutions is a milestone achievement, creditable to the advancements in PONb and POTa synthesis. For example, deposition of aqueous Nb<sub>10</sub> solutions resulted in the formation of electrochromic Nb<sub>2</sub>O<sub>5</sub> films that can function as optical switches for windows.<sup>82–84</sup> These Nb<sub>2</sub>O<sub>5</sub> films can modulate solar radiation transmittance and selectively block



near-infrared and visible light through an applied electrochemical voltage.<sup>82</sup> Prior methods for the deposition of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> films are reliant on sol-gel, sputtering or laser ablation methods, which require the use of harmful precursors, lack reproducibility and are expensive.<sup>35</sup>

For example, prior sol-gel or spray pyrolysis syntheses of potassium sodium niobate (KNN) have used niobium ethoxide,<sup>85,86</sup> or ammonium niobium oxalate,<sup>87,88</sup> to overcome the insolubility of Nb<sub>2</sub>O<sub>5</sub>. Regardless of these metalorganics precursors providing a solution mediated route to KNN, they have the inherent disadvantage of being moisture sensitive. To overcome this challenge, the Nb<sub>6</sub> species has been used to deposit KNN thin films from aqueous solutions,<sup>89–91</sup> while also obviating the need for harmful precursors conventionally used in the solid-state synthesis of niobate films.<sup>91</sup> Furthermore, using the PONb as molecular building blocks bodes well for facilitating *in situ* monitoring of the formation crystalline niobates, from an amorphous precursor, with selectivity and stoichiometric control.<sup>59</sup> This is advantageous when considering the low coefficient of thermal expansion of niobates, and is beneficial to studies aimed at elucidating negative thermal expansion in ceramic materials.<sup>92</sup>

Fabrication of alkali-free Ta<sub>2</sub>O<sub>5</sub> thin films was possible through deposition of aqueous Ta<sub>6</sub> and Nb<sub>6</sub> solutions.<sup>93,94</sup> These studies determined that films deposited from aqueous Ta<sub>6</sub> solutions would always yield atomically smooth Ta<sub>2</sub>O<sub>5</sub> films, whereas the isostructural Nb<sub>6</sub> would not form smooth Nb<sub>2</sub>O<sub>5</sub> films. The synthesis of Ta<sub>6</sub>, however, in these studies was limited by use of the moisture sensitive TaCl<sub>5</sub> as the Ta<sub>2</sub>O<sub>5</sub> source<sup>94</sup> – similarly to the initial Nb<sub>10</sub> synthesis by Graeber and Morosin that used niobium pentaethoxide.<sup>19</sup> The alkali-free synthesis of Ta<sub>6</sub> was improved later on *via* the use of tantalum acid and microwave irradiation, to circumvent the use of TaCl<sub>5</sub> as a Ta<sub>2</sub>O<sub>5</sub> source.<sup>16</sup> Prior to the development of the microwave synthesis of Ta<sub>6</sub>, only the synthesis of the novel titanium-substituted POTa had used tantalum acid to replace use of TaCl<sub>5</sub>.<sup>48</sup> Tantalum pentachloride, nonetheless, has proven useful as a Ta<sub>2</sub>O<sub>5</sub> source for the synthesis of alkali-free Ta<sub>6</sub>, used in the electrochemical deposition of electrochromic Ta<sub>2</sub>O<sub>5</sub> thin films.<sup>95</sup>

Along with the improved synthetic procedures for PONb and POTa came concomitant investigations in the application of these POMs. For example, Nb<sub>6</sub> which is stable at pH ≥ 10 was determined to be viable as a potential base catalyst in the degradation of the nerve agent diisopropyl fluorophosphate.<sup>96</sup> The PONb–POV cluster ([PNb<sub>12</sub>O<sub>40</sub>(V<sup>V</sup>O)<sub>2</sub>(V<sup>IV</sup>O<sub>12</sub>)]<sup>25–</sup>) has also demonstrated the capacity to catalyse the hydrolysis of the nerve agent diethyl cyanophosphate.<sup>97</sup> The influence of the Nb<sub>10</sub> cluster on calcium homeostasis was determined to be stronger than monomeric vanadate, molybdate and tungstate.<sup>98</sup> The isostructural decametallates, Nb<sub>10</sub> and TiNb<sub>9</sub>, have also been used as models to inhibit amyloid aggregation that is consistent with certain neurodegenerative (Alzheimer's) diseases.<sup>99</sup> Note this finding was possible due to prior studies in determining the aqueous stability of Nb<sub>10</sub> and TiNb<sub>9</sub>,<sup>17,40</sup> which established reproducible PONb syntheses.<sup>44,46–52</sup> These

are among the array of examples which highlights the possibility of using PONb in biological models for probing cellular processes.

Still on the matter of heterometal niobates, the initial introduction of the Cr<sup>3+</sup> ion into the PONb structure ([Cr<sub>2</sub>(OH)<sub>4</sub>Nb<sub>10</sub>O<sub>30</sub>]<sup>8–</sup>) ushered in a strategy for extending the visible absorbance of PONb, to provide possible photochemical properties.<sup>49</sup> This correlated to the subsequent inclusion of the Cr<sup>3+</sup> (CrNb<sub>9</sub>), Mn<sup>2+</sup> (MnNb<sub>9</sub>), Fe<sup>3+</sup> (FeNb<sub>9</sub>), Co<sup>2+</sup> (CoNb<sub>9</sub>) and Ni<sup>2+</sup> (NiNb<sub>9</sub>) ions into the Nb<sub>10</sub> framework – *via* site specific substitution of a Nb(v) atom – similarly to the TiNb<sub>9</sub> ion in previous studies.<sup>50,52</sup>

These heterometal-substituted Nb<sub>10</sub> structures possessed photocatalytic properties due to them promoting H<sub>2</sub> evolution in methanol–water mixtures.<sup>52</sup> In addition, Pt-modified films with Nb<sub>6</sub> scrolls in methanol–water mixtures exhibited photocatalytic activity *via* H<sub>2</sub> evolution similarly.<sup>100</sup> Photocatalytic properties were also exhibited by the tellurium PONb species [H<sub>2</sub>TeNb<sub>5</sub>O<sub>19</sub>]<sup>5–</sup>.<sup>101</sup> Fabrication of phosphoniobate patterned thin films was also possible from aqueous peroxophosphoniobate solutions of [HNb<sub>4</sub>P<sub>2</sub>O<sub>14</sub>(O<sub>2</sub>)<sub>4</sub>]<sup>5–</sup>, and [H<sub>7</sub>Nb<sub>6</sub>P<sub>4</sub>O<sub>24</sub>(O<sub>2</sub>)<sub>6</sub>]<sup>3–</sup>, which bodes well for the development of semiconductor films.<sup>102</sup> Another niobium–phosphate cluster [Nb<sub>9</sub>P<sub>5</sub>O<sub>41</sub>]<sup>9–</sup> reacts with H<sub>2</sub>O<sub>2</sub> and shows potential for industrial applications.<sup>47</sup> Application of Nb<sub>6</sub>, synthesised *via* niobic acid, has also been used for direct CO<sub>2</sub> capture from aqueous solutions,<sup>103</sup> and this further reiterates the benefit of niobic acid in probing the solution chemistry of niobium.

## Conclusions and perspectives

PONb offer both selectivity and stoichiometric control in the synthesis of niobium species, whether through the standard isopolyanions or *via* heterometal substitution/inclusion. Leveraging this ability can create the opportunity to fabricate niobates in the solid-state, which otherwise could prove more challenging *via* alternative approaches. We can see how historically there was a limitation in the niobium and tantalum species accessible through the use of HF solutions, or the molten salt approach. Neither of the aforementioned reactions are commonplace for replicating under standard conditions due to their inherent risks; especially a molten salt process which can be difficult to contain. More so, it is due to the dissolution of niobium and tantalum species under these conditions which promulgated the convention that they are sluggish to react, which made exploration of their solution chemistry stagnate in comparison to the group VI metals.

On this premise it is plausible that this idea continues to be reiterated among other natural scientists (geologists, chemists, physicists *etc.*), and it feeds the notion that oxides of niobium and tantalum are inadvertently unreactive. With the advancements in synthesis of PONb and POTa we know the preceding assumption is an exaggeration. Rather, it is the conditions (pH, presence of strongly coordinating ions) which largely influence the dissolution to yield POMs. Altering the



conditions which favour stabilisation of the respective POMs, similarly influence the aggregation processes of niobium and tantalum POM species.

Outside of synthetic advancements, such as the synthesis of aggregated Ta<sub>6</sub> structures, heterometal substituted POTa (titanotantalates), or the fabrication of solid-state Ta<sub>2</sub>O<sub>5</sub> thin films from aqueous Ta<sub>6</sub> solutions; the expansion of the POTa field has remained limited compared to the PONb. Perhaps this is partially due to the lack of commercially available tantalic acid as a precursor in POTa synthesis, to minimise use of moisture sensitive reagents. Furthermore, the inability to synthesise other isopolyanions of tantalum in aqueous medium thus far – such as Ta<sub>10</sub> – exacerbates the latter effect. The absence of investigations into the solution chemistry of Ta<sub>10</sub> has essentially restricted the solution chemistry of tantalum(v) to pH ≥ 10; *i.e.* the Ta<sub>6</sub>. Therefore, information regarding the pH stability of Ta<sub>10</sub>, or whether it dissociates to Ta<sub>6</sub> *via* intermediary species, remains unknown until the aqueous synthesis is established.

More so, discerning how larger POTa structures (>10 Ta atoms) are assembled is similarly challenged, because the library of aqueous synthesised POTa is limited to the single isopolyanion, *i.e.* Ta<sub>6</sub>. It would be myopic to assume that understanding the intricacy of this process bears no significance to interpreting solid-state dissolution (*or lack thereof*) of tantalum oxides. For example, in geochemical processes related to tantalum in the natural environment, that are relevant to radionuclide leaching. The studies into the solution chemistry of Nb<sub>10</sub> provided a wealth of information on niobium(v) solution chemistry and this has contributed to a better understanding of niobium oxide in the solid state. Hence with a similar understanding of tantalum(v) solution chemistry, it is plausible that application of tantalum oxide – and by extension tantalum – in the solid-state could be improved.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

## Acknowledgements

M. A. R. acknowledges the financial support of the Knut & Alice Wallenberg Foundation, Magnus Bergvalls Stiftelse (PANLA: 2024-453) and The Royal Swedish Academy of Sciences (PANLA: ES2023-0007). The Wenner-Gren Foundations (RSv2024-0038), The Crafoord Foundation (REEP: 20240831) and the Royal Physiographic Society in Lund

(43726) are also acknowledged for financial support. M. A. R. thanks Prof. Kimberly Dick Thelander (Lund University) for enriching scientific discourse and mentorship. Finally, Assoc. Prof. C. André Ohlin (Umeå University) is acknowledged for years of fruitful discussions, teaching scientific “Billisims” (*a colloquial term for skepticism*), and for an introduction to polyoxoniobate and polyoxotantalate chemistry.

## References

- 1 L.-Y. Sun, X. Liu, X. Xu, S.-W. Lei, H.-G. Li and Q.-J. Zhai, *J. Iron Steel Res. Int.*, 2022, **29**, 1513–1525.
- 2 C. Chaneliere, J. L. Autran, R. A. B. Devine and B. Balland, *Mater. Sci. Eng., R*, 1998, **22**, 269–322.
- 3 V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P.-L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon and B. Dunn, *Nat. Mater.*, 2013, **12**, 518–522.
- 4 H. Matsuno, A. Yokoyama, F. Watari, M. Uo and T. Kawasaki, *Biomaterials*, 2001, **22**, 1253–1262.
- 5 M. Nyman, *Dalton Trans.*, 2011, **40**, 8049–8058.
- 6 H.-Y. Zhao, Y.-Z. Li, J.-W. Zhao, L. Wang and G.-Y. Yang, *Coord. Chem. Rev.*, 2021, **443**, 213966.
- 7 Z. Yang, J. Li, J. Niu and J. Wang, *Dalton Trans.*, 2023, **52**, 4632–4642.
- 8 N. I. Gumerova, A. Prado-Roller, M. A. Rambaran, C. A. Ohlin and A. Rompel, *Inorg. Chem.*, 2021, **60**, 12671–12675.
- 9 M. T. Pope, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Pergamon, Oxford, 2003, pp. 635–678.
- 10 M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34–48.
- 11 W. N. Lipscomb, *Inorg. Chem.*, 1965, **4**, 132–134.
- 12 J. C. Bailar Jr, H. Booth and M. Grennert, *Inorg. Synth.*, 1939, **1**, 132–133.
- 13 M. Aureliano, C. A. Ohlin, M. O. Vieira, M. P. M. Marques, W. H. Casey and L. A. B. De Carvalho, *Dalton Trans.*, 2016, **45**, 7391–7399.
- 14 S. Mallik, S. S. Dash, K. M. Parida and B. K. Mohapatra, *J. Colloid Interface Sci.*, 2006, **300**, 237–243.
- 15 J. A. Dias, S. C. L. Dias, E. Caliman, J. Bartis and L. Francesconi, in *Inorganic Syntheses*, 2014, vol. 36, pp. 210–217.
- 16 M. A. Rambaran, M. Pascual-Borràs and C. A. Ohlin, *Eur. J. Inorg. Chem.*, 2019, **2019**, 3913–3918.
- 17 E. M. Villa, C. A. Ohlin, E. Balogh, T. M. Anderson, M. D. Nyman and W. H. Casey, *Angew. Chem., Int. Ed.*, 2008, **47**, 4844–4846.
- 18 A. Agulyansky, in *Chemistry of Tantalum and Niobium Fluoride Compounds*, ed. A. Agulyansky, Elsevier Science, Amsterdam, 2004, pp. 253–338.
- 19 E. J. Graeber and B. Morosin, *Acta Crystallogr., Sect. B*, 1977, **33**, 2137–2143.
- 20 T. Mokkelbost, Ø. Andersen, R. A. Strøm, K. Wiik, T. Grande and M.-A. Einarsrud, *J. Am. Ceram. Soc.*, 2007, **90**, 3395–3400.



- 21 T. M. Alam, M. Nyman, B. R. Cherry, J. M. Segall and L. E. Lybarger, *J. Am. Chem. Soc.*, 2004, **126**, 5610–5620.
- 22 T. M. Anderson, S. G. Thoma, F. Bonhomme, M. A. Rodriguez, H. Park, J. B. Parise, T. M. Alam, J. P. Larentzos and M. Nyman, *Cryst. Growth Des.*, 2007, **7**, 719–723.
- 23 M. Nyman, T. M. Alam, F. Bonhomme, M. A. Rodriguez, C. S. Frazer and M. E. Welk, *J. Cluster Sci.*, 2006, **17**, 197–219.
- 24 D. Sures, M. Segado, C. Bo and M. Nyman, *J. Am. Chem. Soc.*, 2018, **140**, 10803–10813.
- 25 A. Gorzsás, I. Andersson and L. Pettersson, *J. Inorg. Biochem.*, 2009, **103**, 517–526.
- 26 G. Rayner-Canham and Z. Zheng, *Found. Chem.*, 2008, **10**, 13–18.
- 27 R. D. Hall and E. F. Smith, *J. Am. Chem. Soc.*, 1905, **27**, 1369–1403.
- 28 C. W. Balke and E. F. Smith, *J. Am. Chem. Soc.*, 1908, **30**, 1637–1668.
- 29 H. T. S. Britton and R. A. Robinson, *J. Chem. Soc.*, 1932, 2265–2270.
- 30 F. Windmaisser, *Z. Anorg. Allg. Chem.*, 1941, **248**, 283–288.
- 31 I. Lindqvist, *Ark. Kemi*, 1953, **5**, 247–250.
- 32 J. E. Guerschai and B. Spinner, *Bull. Soc. Chim. Fr.*, 1965, 1122–1124.
- 33 D. Zhang, Z. Liang, S. Liu, L. Li, P. Ma, S. Zhao, H. Wang, J. Wang and J. Niu, *Inorg. Chem.*, 2017, **56**, 5537–5543.
- 34 T. M. Anderson, M. A. Rodriguez, F. Bonhomme, J. N. Bixler, T. M. Alam and M. Nyman, *Dalton Trans.*, 2007, 4517–4522.
- 35 M. A. Rambaran, A. Gorzsás, M. Holmboe and C. A. Ohlin, *Dalton Trans.*, 2021, **50**, 16030–16038.
- 36 G. R. Lee and J. A. Crayston, *J. Mater. Chem.*, 1996, **6**, 187–192.
- 37 W. G. Klemperer and K. A. Marek, *Eur. J. Inorg. Chem.*, 2013, **2013**, 1762–1771.
- 38 E. M. Villa, C. A. Ohlin, E. Balogh, T. M. Anderson, M. D. Nyman and W. H. Casey, *Am. J. Sci.*, 2008, **308**, 942–953.
- 39 J. R. Black, M. Nyman and W. H. Casey, *J. Am. Chem. Soc.*, 2007, **129**, 5298–5298.
- 40 E. M. Villa, C. A. Ohlin and W. H. Casey, *J. Am. Chem. Soc.*, 2010, **132**, 5264–5272.
- 41 E. M. Villa, C. A. Ohlin, J. R. Rustad and W. H. Casey, *J. Am. Chem. Soc.*, 2009, **131**, 16488–16492.
- 42 M. Nyman, F. Bonhomme, T. M. Alam, M. A. Rodriguez, B. R. Cherry, J. L. Krumhansl, T. M. Nenoff and A. M. Sattler, *Science*, 2002, **297**, 996–998.
- 43 M. Nyman, L. J. Criscenti, F. Bonhomme, M. A. Rodriguez and R. T. Cygan, *J. Solid State Chem.*, 2003, **176**, 111–119.
- 44 C. A. Ohlin, E. M. Villa and W. H. Casey, *Inorg. Chim. Acta*, 2009, **362**, 1391–1392.
- 45 C. A. Ohlin, E. M. Villa, J. C. Fettinger and W. H. Casey, *Dalton Trans.*, 2009, 2677–2678.
- 46 J.-H. Son and W. H. Casey, *Dalton Trans.*, 2013, **42**, 13339–13342.
- 47 J.-H. Son and W. H. Casey, *Chem. Commun.*, 2015, **51**, 12744–12747.
- 48 J.-H. Son and W. H. Casey, *Chem. – Eur. J.*, 2016, **22**, 14155–14157.
- 49 J.-H. Son, C. A. Ohlin and W. H. Casey, *Dalton Trans.*, 2012, **41**, 12674–12677.
- 50 J.-H. Son, C. A. Ohlin and W. H. Casey, *Dalton Trans.*, 2013, **42**, 7529–7533.
- 51 J.-H. Son and W. H. Casey, *Dalton Trans.*, 2015, **44**, 20330–20333.
- 52 J.-H. Son, J. Wang and W. H. Casey, *Dalton Trans.*, 2014, **43**, 17928–17933.
- 53 M. Pascual-Borràs, X. López, A. Rodríguez-Fortea, R. J. Errington and J. M. Poblet, *Chem. Sci.*, 2014, **5**, 2031–2042.
- 54 R. Sharma, J. Zhang and C. A. Ohlin, *Phys. Chem. Chem. Phys.*, 2016, **18**, 8235–8241.
- 55 C. A. Ohlin and W. H. Casey, in *Annual Reports on NMR Spectroscopy*, ed. G. A. Webb, Academic Press, 2018, vol. 94, pp. 187–248.
- 56 C. A. Ohlin, *Chem. – Asian J.*, 2012, **7**, 262–270.
- 57 E. Balogh, T. M. Anderson, J. R. Rustad, M. Nyman and W. H. Casey, *Inorg. Chem.*, 2007, **46**, 7032–7039.
- 58 C. A. Ohlin, E. M. Villa, J. R. Rustad and W. H. Casey, *Nat. Mater.*, 2010, **9**, 11–19.
- 59 M. A. Rambaran, D. Jacobsson, S. Lehmann and K. A. Dick, *Chem. – Eur. J.*, 2025, **31**, e202404417.
- 60 M. Matsumoto, Y. Ozawa and A. Yagasaki, *Inorg. Chem. Commun.*, 2011, **14**, 115–117.
- 61 M. Matsumoto, Y. Ozawa, A. Yagasaki and Y. Zhe, *Inorg. Chem.*, 2013, **52**, 7825–7827.
- 62 M. Matsumoto, Y. Ozawa and A. Yagasaki, *Inorg. Chem.*, 2012, **51**, 5991–5993.
- 63 M. Maekawa, Y. Ozawa and A. Yagasaki, *Inorg. Chem.*, 2006, **45**, 9608–9609.
- 64 M. Matsumoto, Y. Ozawa and A. Yagasaki, *Polyhedron*, 2010, **29**, 2196–2201.
- 65 C. A. Ohlin, E. M. Villa, J. C. Fettinger and W. H. Casey, *Angew. Chem., Int. Ed.*, 2008, **47**, 8251–8254.
- 66 K. Sahel, L. Elsellami, I. Mirali, F. Dappozze, M. Bouhent and C. Guillard, *Appl. Catal., B*, 2016, **188**, 106–112.
- 67 R. J. Wilbraham, C. Boxall, D. T. Goddard, R. J. Taylor and S. E. Woodbury, *J. Nucl. Mater.*, 2015, **464**, 86–96.
- 68 M. Nyman, C. R. Powers, F. Bonhomme, T. M. Alam, E. J. Maginn and D. T. Hobbs, *Chem. Mater.*, 2008, **20**, 2513–2521.
- 69 M. Nyman, A. Tripathi, J. B. Parise, R. S. Maxwell and T. M. Nenoff, *J. Am. Chem. Soc.*, 2002, **124**, 1704–1713.
- 70 F. E. Osterloh, *Chem. Mater.*, 2008, **20**, 35–54.
- 71 T. Rahman, E. Petrus, M. Segado, N. P. Martin, L. N. Palys, M. A. Rambaran, C. A. Ohlin, C. Bo and M. Nyman, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117839.
- 72 E. M. Villa, C. A. Ohlin and W. H. Casey, *Chem. – Eur. J.*, 2010, **16**, 8631–8634.
- 73 H. Friis and W. H. Casey, *Can. Mineral.*, 2018, **56**, 905–912.



- 74 H. Friis, A. O. Larsen, A. R. Kampf, R. J. Evans, R. S. Selbekk, A. Sánchez and J. Kihle, *Eur. J. Mineral.*, 2014, **26**, 567–576.
- 75 H. Friis, M. T. Weller and A. R. Kampf, *Mineral. Mag.*, 2017, **81**, 543–554.
- 76 M. B. Andrade, D. Atencio, L. A. D. M. Filho and J. Spratt, *Mineral. Mag.*, 2018, **82**, 111–120.
- 77 J. Niu, P. Ma, H. Niu, J. Li, J. Zhao, Y. Song and J. Wang, *Chem. – Eur. J.*, 2007, **13**, 8739–8748.
- 78 N. P. Martin, E. Petrus, M. Segado, A. Arteaga, L. N. Zakharov, C. Bo and M. Nyman, *Chem. – Eur. J.*, 2019, **25**, 10580–10584.
- 79 P. Huang, C. Qin, Z.-M. Su, Y. Xing, X.-L. Wang, K.-Z. Shao, Y.-Q. Lan and E.-B. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 14004–14010.
- 80 R. Tsunashima, D.-L. Long, H. N. Miras, D. Gabb, C. P. Pradeep and L. Cronin, *Angew. Chem., Int. Ed.*, 2010, **49**, 113–116.
- 81 H. Friis, A. R. Kampf and M. T. Weller, *Mineral. Mag.*, 2017, **81**, 543–554.
- 82 A. Llordés, G. Garcia, J. Gazquez and D. J. Milliron, *Nature*, 2013, **500**, 323–326.
- 83 A. Llordés, A. T. Hammack, R. Buonsanti, R. Tangirala, S. Aloni, B. A. Helms and D. J. Milliron, *J. Mater. Chem.*, 2011, **21**, 11631–11638.
- 84 A. Llordés, Y. Wang, A. Fernandez-Martinez, P. Xiao, T. Lee, A. Poulain, O. Zandi, C. A. Saez Cabezas, G. Henkelman and D. J. Milliron, *Nat. Mater.*, 2016, **15**, 1267–1273.
- 85 J.-C. Grivel, K. Thydén, J. R. Bowen and A. B. Haugen, *Thin Solid Films*, 2018, **650**, 7–10.
- 86 A. D. Handoko and G. K. L. Goh, *CrystEngComm*, 2013, **15**, 672–678.
- 87 A. B. Haugen, *Ceramics*, 2019, **2**, 460–471.
- 88 N. Helth Gaukås, S. M. Dale, T. M. Raeder, A. Toresen, R. Holmestad, J. Glaum, M. A. Einarsrud and T. Grande, *Materials*, 2019, **12**, 2042.
- 89 D. Fast, M. Clark, L. Fullmer, K. Grove, M. Nyman, B. Gibbons and M. Dolgos, *Thin Solid Films*, 2020, **710**, 138270.
- 90 T. Rahman, N. P. Martin, J. K. Jenkins, R. Elzein, D. B. Fast, R. Addou, G. S. Herman and M. Nyman, *Inorg. Chem.*, 2022, **61**, 3586–3597.
- 91 M. Nyman, T. Rahman and I. Colliard, *Acc. Chem. Res.*, 2023, **56**, 3616–3625.
- 92 M. J. Dejneka, C. L. Chapman and S. T. Mixture, *J. Am. Ceram. Soc.*, 2011, **94**, 2249–2261.
- 93 L. B. Fullmer, R. H. Mansergh, L. N. Zakharov, D. A. Keszler and M. Nyman, *Cryst. Growth Des.*, 2015, **15**, 3885–3892.
- 94 R. H. Mansergh, L. B. Fullmer, D.-H. Park, M. Nyman and D. A. Keszler, *Chem. Mater.*, 2016, **28**, 1553–1558.
- 95 C. A. Saez Cabezas, K. Miller, S. Heo, A. Dolocan, G. LeBlanc and D. J. Milliron, *Chem. Mater.*, 2020, **32**, 4600–4608.
- 96 M. K. Kinnan, W. R. Creasy, L. B. Fullmer, H. L. Schreuder-Gibson and M. Nyman, *Eur. J. Inorg. Chem.*, 2014, **2014**, 2361–2367.
- 97 J. Dong, J. Hu, Y. Chi, Z. Lin, B. Zou, S. Yang, C. L. Hill and C. Hu, *Angew. Chem., Int. Ed.*, 2017, **56**, 4473–4477.
- 98 G. Fraqueza, C. A. Ohlin, W. H. Casey and M. Aureliano, *J. Inorg. Biochem.*, 2012, **107**, 82–89.
- 99 H. Chaudhary, I. A. Iashchishyn, N. V. Romanova, M. A. Rambaran, G. Musteikyte, V. Smirnovas, M. Holmboe, C. A. Ohlin, Ž. M. Svedružić and L. A. Morozova-Roche, *ACS Appl. Mater. Interfaces*, 2021, **13**, 26721–26734.
- 100 B. N. Nunes, C. Haisch, A. V. Emeline, D. W. Bahnemann and A. O. T. Patrocínio, *Catal. Today*, 2019, **326**, 60–67.
- 101 J.-H. Son, J. Wang, F. E. Osterloh, P. Yu and W. H. Casey, *Chem. Commun.*, 2014, **50**, 836–838.
- 102 J.-H. Son, D.-H. Park, D. A. Keszler and W. H. Casey, *Chem. – Eur. J.*, 2015, **21**, 6727–6731.
- 103 Z. Mao, M. Rashwan, E. Garrido Ribó, M. Nord, L. N. Zakharov, T. W. Surta, A. Uysal and M. Nyman, *J. Am. Chem. Soc.*, 2024, **146**, 19489–19498.

