

Inorganic Chemistry

Distinctive Interactions of Cesium and Hexaniobate in Water

Dylan J. Sures,^[a] Sulata K. Sahu,^[b, c] Pedro I. Molina,^[a] Alexandra Navrotsky,^[b] and May Nyman^{*[a]}

The Cs-effect states Cs⁺ has more covalent character in bonding interactions than the lighter alkalis. It is exploited in organic synthesis and influences behavior in water, most notably radioactive ¹³⁷Cs in nuclear wastes or the environment. Niobium polyoxometalates (Nb-POMs) provide a unique opportunity to probe aqueous phase ion-pairing responsible for cesium's solution behavior, because Nb-POMs are most soluble in conditions of maximum ion-association. Moreover, POMs broadly resemble metal-oxide surfaces representative of interfaces found in the environment and industrial processes. Aqueous dissolution calorimetry reveals that Cs–Nb-POM exhibits great-

er concentration dependence in its endothermic dissolution, compared to the lighter alkali analogues. This phenomenon is attributed to persistent ion-pairs upon dissolution, even in very dilute and otherwise ion-free solutions. While dissociation of these cation-anion interactions in the crystalline lattice is the dominant endothermic step of dissolution, deprotonation of the Nb-POM is the most exothermic. These studies highlight the importance of the competing effects of aqueous ion association and acid-base chemistry that control solubility of compounds from simple oxoanions to metal-oxo clusters to supra-molecular assemblies to solid metal oxides.

Introduction

Cesium departs from Group IA character: it is the only alkali with frontier f-orbitals and is the largest metal cation on the periodic table in its common oxidation state. These characteristics may play a role in the 'Cs-effect', the efficacy of cesium salts to catalyze organic reactions, where the lighter alkalis are not nearly so effective.^[1] The stoichiometric or catalytic role of Cs⁺ in such reactions is not well-understood and explanations include its ability to pre-organize reactants due to strong ion-association and bonding behavior, or simply possessing higher solubility in organic solvents. In addition, the ¹³⁷Cs⁺ radioisotope has attracted considerable attention and concern as the most mobile radionuclide in liquid and solid nuclear wastes and spent nuclear fuel, both in controlled materials^[2] and uncontrolled contamination^[3] in the environment. More recently, the Fukushima accident has produced widespread Cs-contamination in soil, seawater, and groundwater.^[4] It is therefore important to understand Cs's solution behavior, especially ion-association and bonding, in order to achieve separation from

Na⁺ and K⁺, which are far more abundant in the natural environment and nuclear wastes. Technologies that separate Cs⁺ from Na⁺ in nuclear wastes exploit precipitation of poorly soluble Cs⁺ salts^[5] or Cs⁺-selective ion exchangers.^[6] The partial covalent bonding character of Cs⁺ leading to strong ion-association in solution and at interfaces is likely an important factor in the efficacy of these technologies.

Ion-association in water is particularly complex: it is affected by the concomitant organization of water molecules, self-buffering behavior (binding and releasing protons) of dissolved oxo-species, and the presence of multiple ion types, particularly in complex, natural and/or fluctuating systems.^[7] Ion-association affects phenomena ranging from the aforementioned chemical reactivity and transport of ions in nature to dissolution of metal oxides. More broadly, ion-association controls organization of biological and inorganic macromolecules, and other supra-molecular assembly processes. Polyoxometalates (POMs, discrete, anionic metal-oxo clusters of Groups V and VI d⁰ metals) offer a unique opportunity to investigate ion-association because the clusters can be synthesized with any counter-cation, providing a controlled series of compounds.^[8] Additionally, they are intermediate in size between infinite metal oxide lattices and simple oxoanions and hence they possess characteristics of each. Additionally, POMs are considered model metal oxide surfaces, and useful for computational and experimental studies at the interface. The Cs⁺ salt of [Nb₆O₁₉]⁸⁻ (abbreviated Nb₆, Figure 1), due to both its unusually high water solubility in conditions of maximum ion-association, is especially useful for study.^[9] The solubility trend of Nb₆ and most Nb-POMs is opposite to that of all other polyoxoanions including Group VI POMs and the uranyl peroxide clusters,^[10] as well as that of anionic colloids and proteins, in accordance with the Hofmeister series.^[11] To better understand the atomic level interrelated phe-

[a] D. J. Sures, Dr. P. I. Molina, Prof. M. Nyman
Department of Chemistry, Oregon State University
Corvallis, OR 97331; nyman.chem.oregonstate.edu
E-mail: may.nyman@oregonstate.edu

[b] Dr. S. K. Sahu, Prof. A. Navrotsky
Peter A. Rock Thermochemistry Laboratory and Nanomaterials in the
Environment, Agriculture, and Technology Organized Research Unit;
navrotsky.engr.ucdavis.edu
University of California Davis, Davis, CA 95616

[c] Dr. S. K. Sahu
Department of Materials Science & Engineering, Massachusetts Institute
of Technology, Cambridge, MA 02139

Supporting information for this article is available on the WWW under
<http://dx.doi.org/10.1002/slct.201600493>

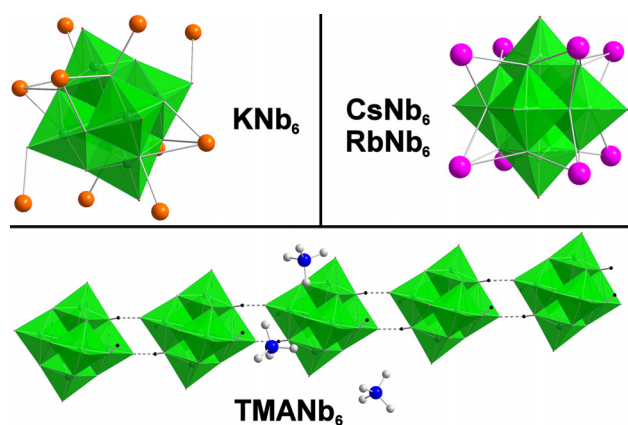


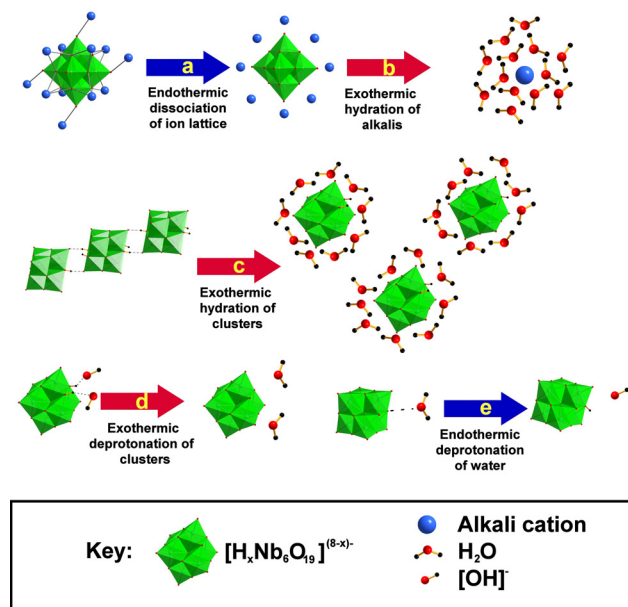
Figure 1. Solid-state bonding of Nb_6 with K^+ (top left, orange), Cs^+ or Rb^+ (top right, magenta) and TMA^+ (bottom) counter-cations. The lattermost case exhibits cluster linking via hydrogen bonding of the $[\text{H}_3\text{Nb}_6\text{O}_{19}]^{5-}$ clusters.^[8a] Green polyhedra are NbO_6 .

nomena of ion-association, acid-base behavior, and solubility; we conducted thermochemical measurements of Nb_6 -POM dissolution. Here we quantify the enthalpy of aqueous dissolution of Cs^+ , Rb^+ , K^+ , Li^+ and tetramethylammonium (TMA^+ , $[\text{CH}_3]_4\text{N}^+$) salts of Nb_6 in both pure water and parent hydroxide solutions. Dissolution in hydroxide represents more controlled conditions that has been prior corroborated with SAXS,^[9] with maximum deprotonation of the clusters and maximum ion-association. Counterintuitively, dissolution in water is more complex with many interrelated processes that are summarized in Scheme 1. This is the first investigation of the dissolution behavior of Nb_6 in pure water. The main finding regarding ion-association shows that the Cs^+ -salt of Nb_6 displays unique concentration-dependent dissolution enthalpy that differs from the other alkalis and also questions prior data that suggest Rb and Cs are similar in aqueous conditions.

Table 1. ΔH_f^{ox} (enthalpy of formation from oxides; $\text{kJ}(\text{mol Nb})^{-1}$) of the alkali hexaniobates and related data

Formula from structure	$\text{Li}_8[\text{Nb}_6\text{O}_{19}] \cdot x\text{H}_2\text{O}$	$\text{K}_8[\text{Nb}_6\text{O}_{19}] \cdot 16\text{H}_2\text{O}^{[8b]}$	$\text{Rb}_8[\text{Nb}_6\text{O}_{19}] \cdot 14\text{H}_2\text{O}^{[8b]}$	$\text{Cs}_8[\text{Nb}_6\text{O}_{19}] \cdot 14\text{H}_2\text{O}^{[8b]}$
H_2O molecules per cluster ^[a]	23.5	16.0	14.1	14.8
Total number (and average per A) of A–O bonds in structure (A = alkali)	No structure available, but related structures ^[13] suggest 40 (avg = 5/ Li^+)	56 (7/ K^+)	62 (7.75/ Rb^+)	68 (8.5/ Cs^+)
$\Delta H_f^{\text{ox}}(\text{kJ}(\text{mol Nb})^{-1})^{[b]}$	-137.2(4.8)	-262.7(5.0)	-279.3(5.9)	-298.7(4.2)
$\Delta H_{\text{ds}}(\text{A}_2\text{O}; \text{kJmol}^{-1})^{[14a-c]}$	-90.3(2.5)	-318.0(3.1)	-332.6(2.2)	-348.9(1.7)
Enthalpy of hydration of A^+ ($\text{kJmol}^{-1})^{[15]}$	-519(3)	-322(3)	-293(3)	-264(3)

[a] Determined from thermogravimetry, [b] Corrected for ΔH_{ds} of lattice water



Scheme 1. Summary of all processes involved in the dissolution of solid Nb_6 clusters in water.

Results and Discussion

As an initial approach, the enthalpy of formation (ΔH_f^{ox}) of the alkali hexaniobates (denoted LiNb_6 , KNb_6 , RbNb_6 and CsNb_6) from their parent oxides (Nb_2O_5 and A_2O) were measured by dissolution into molten sodium molybdate at 700 °C to obtain the enthalpy of drop solution (ΔH_{ds}) (A = alkali; see SI, thermochemical cycles). The Na analogue was not included in the series because it crystallizes from aqueous solution with seven alkali counterions, whereas the other four analogues are all obtained with eight. However, these four analogues are sufficient to reveal series trends. Upon normalization for lattice water, ΔH_f^{ox} for all species are strongly negative, with a trend of increasing exothermicity from Li to Cs (Table 1). The ΔH_f^{ox} of KNb_6 , RbNb_6 and CsNb_6 exhibit a relatively small stepwise difference ($\sim 20 \text{ kJmol}^{-1}$) between the alkali analogues while ΔH_f^{ox} of LiNb_6 is substantially less exothermic. This trend is the same for ΔH_{ds} of A_2O and reflects the greater number of bonds formed by the larger alkalis in the solid-state lattices (Table 1).^[12]

Next, we measured the enthalpy of dissolution (Figure 2) of LiNb_6 , KNb_6 , RbNb_6 and CsNb_6 in water, (ΔH_{dis} , kJmol^{-1} cluster) which is a complex sum of endothermic and exothermic processes (Scheme 1). The main endothermic events include the

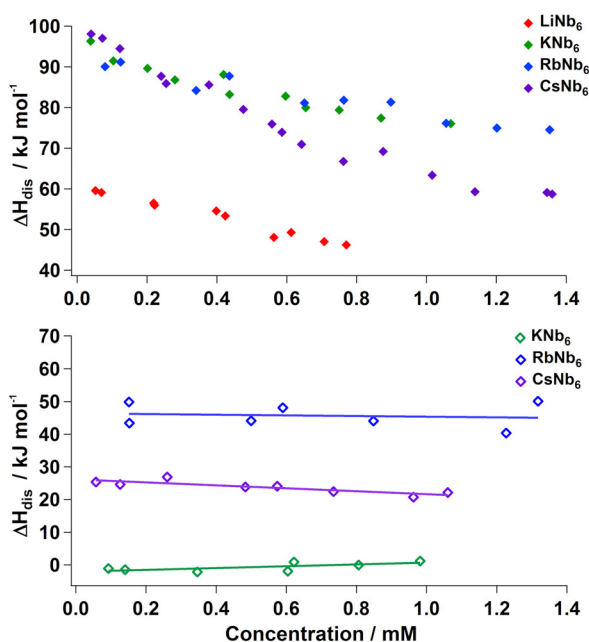
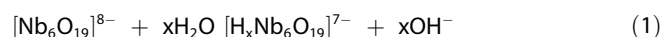


Figure 2. top: Enthalpy of aqueous dissolution (ΔH_{dis}) of LiNb_6 , KNb_6 , RbNb_6 and CsNb_6 in water and **bottom:** in the parent alkali hydroxide (1 M) solutions, normalized for lattice water (i. e. representing dissolution of the dehydrated forms $\text{Li}_8[\text{Nb}_6\text{O}_{19}]$, $\text{K}_8[\text{Nb}_6\text{O}_{19}]$, $\text{Rb}_8[\text{Nb}_6\text{O}_{19}]$ and $\text{Cs}_8[\text{Nb}_6\text{O}_{19}]$; the hydrated enthalpies are shown in figure S1). Trend lines for dissolution in the parent hydroxides are only a guide for the eye.

dissociation of the $\text{A-O}_{\text{cluster}}$ bonds (a) and the hydrogen bonds in the crystal lattice between water molecules with each other and with the oxo-ligands of the clusters (not shown). Exothermic processes (bond formation) include hydration of the dissociated alkalis (b) and of the clusters (c). An additional typical endothermic process upon dissolution of Nb_6 is the protonation of the clusters (e),^[8b,16] which is evidenced by the increase in pH (up to 12, depending on Nb_6 concentration) upon dissolution:



The experimentally observed net effect is endothermic dissolution of all the alkali analogues. LiNb_6 has the least endothermic ΔH_{dis} , likely reflecting the much greater exothermic enthalpy of hydration of Li^+ (Table 1). The endothermic dissolution of all four alkali- Nb_6 salts is due to domination of the endothermic processes of breaking the $\text{A-O}_{\text{cluster}}$ bonds in the lattice and protonation of the basic clusters (Eq. 1). At the lowest concentration measured (~ 0.05 mM), ΔH_{dis} for the K, Rb and Cs analogues when normalized for number of water molecules are very similar (around 90–95 kJ mol^{-1}) and overlap up to 0.4 mM. Since the hydration enthalpies of the alkalis are inherently different and predictable (exothermic: $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+$), as are the measured lattice energies (exothermic: $\text{KNb}_6 < \text{RbNb}_6 < \text{CsNb}_6$), we expect the dissolution-hydration to yield a distinct trend of increasing ΔH_{dis} endothermicity of $\text{KNb}_6 < \text{RbNb}_6 < \text{CsNb}_6$. Therefore, some other phenomena are con-

tributing to the ΔH_{dis} values, producing similarity at lower concentrations. Hence, we revise our dissolution model to suggest that two correlated phenomena — retained alkali- Nb_6 association ($\text{CsNb}_6 > \text{RbNb}_6 > \text{KNb}_6$) and inhibited cluster protonation — reduce endothermicity of ΔH_{dis} , even at very low concentrations, in pure water. Higher concentrations (up to 1.40 mM) reveal a trend towards less endothermic ΔH_{dis} for all four ANb_6 . This indicates that Nb_6 and alkalis are undergoing less correlated cluster-protonation/alkali-cluster dissociation.

The ΔH_{dis} concentration dependence for LiNb_6 , KNb_6 , and RbNb_6 are similar, while CsNb_6 exhibits *greater* concentration dependence (Figure 2). This is particularly surprising, because solid-state structures^[8b] and prior SAXS^[9a] studies indicate greater similarity between RbNb_6 and CsNb_6 . The current study suggests similarity between KNb_6 and RbNb_6 , while CsNb_6 is distinctive. However, we note that this current study is in much different conditions. The current study of dissolution in pure water at very low concentrations that should *not* favor substantial ion-association. Therefore the differences between the alkali salts become more pronounced.

We also measured ΔH_{dis} in the parent alkali hydroxide solutions (1 M) for KNb_6 , RbNb_6 and CsNb_6 (Figure 2), whereas LiNb_6 is too insoluble in LiOH for practical execution. This dissolution medium simplifies the aqueous phase behavior of Nb_6 , as the protonation of the cluster upon dissolution is minimized.^[9a] With great excess of alkalis in solution, ion-association is maximized and independent of cluster concentration, as shown in the prior SAXS studies.^[9] Indeed, there is minimal concentration dependence, with slightly decreasing endothermicity for CsNb_6 , negligible change for RbNb_6 , and very slightly increasing endothermicity for KNb_6 . The values of ΔH_{dis} are considerably more exothermic for all Nb_6 salts in their parent hydroxide solutions than in water, likely due to decreased proton transfer from the water to the cluster upon dissolution (eq. 1). The distinct relationship of ΔH_{dis} with increasing endothermicity $\text{KNb}_6 < \text{CsNb}_6 < \text{RbNb}_6$ is unexpected. Again, the departure from an expected periodic trend of increasing endothermicity ($\text{K} < \text{Rb} < \text{Cs}$) with increasing energy required to dissociate A-O bonds can be related to anomalous behavior of CsNb_6 . Because ΔH_{dis} of CsNb_6 is considerably less endothermic than that of RbNb_6 , we can conclude that the ions remain more associated upon aqueous dissolution and the short range order reminiscent of the solid-state lattice is less disrupted. Again, this distinction was not made in the prior SAXS studies,^[9a] likely due to sensitivity of the technique to differentiate between similar states. For example, Nb_6 associated with anywhere from 4–8 alkalis in solution might look similar by SAXS, as would the average scattering of Nb_6 clusters with different numbers of alkalis associated.

Next we turn our attention to ΔH_{dis} of TMA^+ salts of Nb_6 in both water and its parent hydroxide. While high temperature calorimetry is meaningless due to the organic, combustible counterions, aqueous dissolution calorimetry is valuable to delineate the behavior and role of the alkali counterions in dissolution and to confirm our hypotheses of the observed trends. TMA^+ , being bulkier and less charge-dense than the alkali metal ions, provides both minimal bonding in the lattice and mini-

mal ion-association in solution, and likewise minimal exothermic hydration enthalpy of the cations upon dissolution. The enthalpy of hydration of TMA^+ is $-105.2(2.8) \text{ kJ mol}^{-1}$,^[17] considerably less exothermic than that of alkali cations (Table 1). The ΔH_{dis} of TMA-Nb_6 in both water and TMA hydroxide is exothermic, and becomes slightly less negative with increasing concentration, differing in both features from the dissolution energetics of the alkali salts. The solid-state arrangement of these triprotonated clusters $[\text{H}_3\text{Nb}_6\text{O}_{19}]^{5-}$ is a linear chain (Figure 1), via H-bonding of the protonated faces, owed to the minimal TMA^+ -cluster association during crystallization.^[8a] Prior studies by X-ray scattering also suggest that the association of clusters upon dissolution in water is partially retained and more structuring is observed in solution with increasing concentration.^[8a] This is consistent with decreasing exothermicity as concentration increases, as they retain the H-bonded state with increasing concentration. Dissolution in TMAOH follows the same trend: less negative dissolution enthalpy with higher order of structuring in solution at higher concentrations (Figure 3).

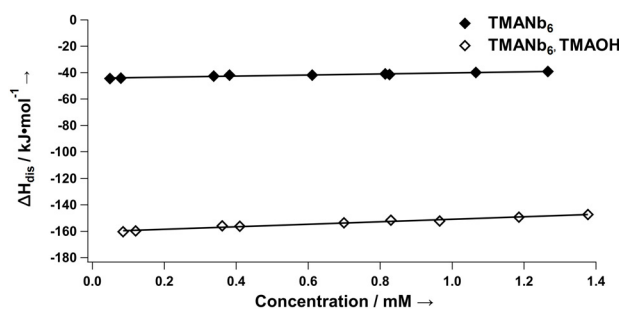
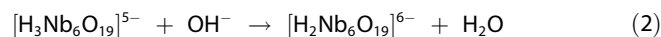


Figure 3. Enthalpy of dissolution of TMANb_6 in water and in 1 M TMAOH .

Overall, ΔH_{dis} is considerably more exothermic in TMAOH than in water. This is because deprotonation of clusters breaks up the hydrogen-bonded cluster chains and therefore a greater degree of exothermic hydration results. Deprotonation of the cluster is a neutralization reaction, which is also exothermic; i.e.:



Conclusions

This data represents the first critical quantitative evaluation of lattice and dissolution energy of water-soluble metal-oxo clusters, and it reveals the correlation between ion-association and acid-base behavior in dissolution processes. The current and follow-on studies of different metal-oxo compositions provides quantitative data that can be correlated with molecular dynamical and density functional theory simulations of these processes. Broadly we conclude that the energy required to dissociate Nb-POM lattices held together by alkali-oxo bonds exceeds energy released upon hydration of the dissociated ions (endothermic dissolution). Conversely, dissolution of alkali-free

lattices held together by only H-oxo bonds is exothermic. Additionally; in conditions where alkali-oxo bonding is retained in solution, formation of H-oxo bond formation is suppressed, and *vice versa*. We will broaden the compositional scope of our thermochemical investigations and delineate the relationship between composition, charge density, and solubility with POMs exhibiting opposite and intermediate solubility trends to that of Nb-POMs (Group VI POMs , uranyl peroxide polyanions, mixed Group V/VI POMs ^[18a,b]). We will also elucidate the fundamental differences between aqueous Ta and Nb chemistries via thermochemistry.^[9b,19] While prior X-ray scattering studies^[9a] and solid-state structure suggested the association of Rb^+ and Cs^+ to Nb_6 is identical, the current technique reveals distinct differences, highlighting the better ability of Cs^+ to retain strong association to an anion in solution and to depart from trends based on periodicity. This we attribute to Cs 's more covalent bonding character, derived from frontier f -orbitals. Moreover, thermochemistry has enabled us to study dissolution processes in very simple solutions containing just the cluster salt and water. We have learned that the deceptively simple solutions represent the most complex dissolution processes, which we will follow-on with ^{133}Cs NMR, UV-vis, SAXS and computational studies. Complementary techniques allow access to different solution conditions and therefore provide a more complete understanding of the fundamental phenomena of acid-base and ion-pairing behavior in water. Charged, water-soluble metal-oxo clusters are excellent models to study ubiquitous processes at the water-metal oxide interface in synthetic, natural and industrial conditions.

There is a Supporting Information document available for this manuscript. Included are tables of drop solution enthalpies, thermochemical cycles, and tables and graphs of hydrated dissolution enthalpies in water and in the parent hydroxide for each alkali hexaniobate. Syntheses, thermogravimetric analysis (TGA) plots, and elemental analyses are also included.

Acknowledgements

DJS and MN acknowledge support by the U.S. Department of Energy, Office of Basic Energy Sciences, Divisions of Materials Sciences and Engineering, under award **DE-SC0010802**. SKS and AN acknowledge support by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical and Geosciences, under award **FG02-97ER14749**.

Keywords: calorimetry · cesium · ion pairs · polyoxometalate · thermochemistry

- [1] a) C. Mayeux, L. Massi, J. F. Gal, L. Charles, P. Burk, *Chem-Eur J* **2014**, *20*, 815–823; b) A. Ostrowicki, E. Koepf, F. Vogtle, *Top Curr Chem* **1992**, *161*, 37–67.
- [2] W. R. Wilmarth, G. J. Lumetta, M. E. Johnson, M. R. Poirier, M. C. Thompson, P. C. Suggs, N. P. Machara, *Solvent Extr Ion Exc* **2011**, *29*, 1–48.
- [3] M. A. Ashraf, S. Akib, M. J. Maah, I. Yusoff, K. S. Balkhair, *Crit Rev Env Sci Tec* **2014**, *44*, 1740–1793.
- [4] Y. H. Koo, Y. S. Yang, K. W. Song, *Prog Nucl Energy* **2014**, *74*, 61–70.

- [5] a) T. Guo, Y. Q. Hu, X. L. Gao, X. S. Ye, H. N. Liu, Z. J. Wu, *Rsc Adv* **2014**, *4*, 24067–24072; b) H. Rogers, J. Bowers, D. Gates-Anderson, *J Hazard Mater* **2012**, *243*, 124–129.
- [6] a) A. J. Celestian, J. D. Kubicki, J. Hanson, A. Clearfield, J. B. Parise, *J Am Chem Soc* **2008**, *130*, 11689–11694; b) A. Tripathi, D. G. Medvedev, M. Nyman, A. Clearfield, *J Solid State Chem* **2003**, *175*, 72–83.
- [7] a) A. M. Stemig, T. A. Do, V. M. Yuwono, W. A. Arnold, R. Lee, *Penn, Environ. Sci. Nano.* **2014**, *1*, 478–487; b) E. H. Oelkers, *Geochim. Cosmochim. Acta* **2001**, *65*, 3703–3718; c) M.A. Blesa, A.D. Weisz, P.J. Morando, J.A. Salfity, G.E. Magaz, A. E. Regazzoni, *Coord. Chem. Rev.* **2000**, *196*, 31–63; d) J. Baumgartner, A. Dey, P. H. H. Bomans, C. Le Coadou, P. Fratzl, N. A. J. M. Sommerdijk, D. Faivre, *Nat. Mater.* **2013**, *12*, 310–314
- [8] a) L. B. Fullmer, R. H. Mansergh, L. N. Zakharov, D. A. Keszler, M. Nyman, *Cryst Growth Des* **2015**, *15*, 3885–3892; b) M. Nyman, T. M. Alam, F. Bonhomme, M. A. Rodriguez, C. S. Frazer, M. E. Welk, *J Clust Sci* **2006**, *17*, 197–219.
- [9] a) M. R. Antonio, M. Nyman, T. M. Anderson, *Angew Chem Int Edit* **2009**, *48*, 6136–6140; b) L. B. Fullmer, P. I. Molina, M. R. Antonio, M. Nyman, *Dalton Trans.* **2014**, *43*, 15295–15299.
- [10] a) Y. Hou, M. Nyman, M. A. Rodriguez, *Angew Chem Int Edit* **2011**, *50*, 12514–12517; b) M. Nyman, P. C. Burns, *Chem Soc Rev* **2012**, *41*, 7354–7367.
- [11] T. Oncsik, G. Trefalt, M. Borkovec, I. Szilagy, *Langmuir* **2015**, *31*, 3799–3807.
- [12] a) S. K. Sahu, S. Zlotnik, A. Navrotsky, P. M. Vilarinho, *J. Mater. Chem. C* **2015**, *3*, 7691–7698; b) S. Zlotnik, S. K. Sahu, A. Navrotsky, P. M. Vilarinho, *Chem. - Eur. J.* **2015**, *21*, 5231–5237; c) A. Navrotsky, *J. Am. Ceram. Soc.* **2014**, *97*, 3349–3359.
- [13] a) T. M. Anderson, S. G. Thoma, F. Bonhomme, M. A. Rodriguez, H. Park, J. B. Parise, T. M. Alam, J. P. Larentzos, M. Nyman, *Cryst Growth Des* **2007**, *7*, 719–723; b) Y. Hou, D. B. Fast, R. E. Ruther, J. M. Amador, L. B. Fullmer, S. R. Decker, L. N. Zakharov, M. R. Dolgos, M. Nyman, *J Solid State Chem* **2015**, *221*, 418–425.
- [14] a) J. M. McHale and A. Navrotsky, *Chem. Mater.* **1997**, *9*, 1538–1546; b) A. Mielewczyk-Gryn, S. Wachowsky, K. I. Lilova, X. Guo, M. Gazda, A. Navrotsky, *Ceram. Int.* **2015**, *41*, 2128–2133; c) S. V. Ushakov, A. Navrotsky, J. M. Farmer, L.A. Boatner, *J. Mater. Res.* **2004**, *19*, 2165–2175.
- [15] D. W. Smith, *J. Chem. Ed.* **1977**, *54*, 540–542.
- [16] M. K. Kinnan, W. R. Creasy, L. B. Fullmer, H. L. Schreuder-Gibson, M. Nyman, *Eur J Inorg Chem* **2014**, *2014*, 2361–2367.
- [17] Y. Nagano, M. Sakiyama, T. Fujiwara, Y. Kondo, *J Phys Chem-US* **1988**, *92*, 5823–5827.
- [18] a) P. I. Molina, D. J. Sures, P. Miró, L. N. Zakharov, M. Nyman, *Dalton Trans.* **2015**, *44*, 15813–15822; b) D. J. Sures, P. I. Molina, P. Miró, L. N. Zakharov, M. Nyman, *New J. Chem.* **2016**, *40*, 928–936.
- [19] G. J. P. Deblonde, N. Delaunay, D. Lee, A. Chagnes, G. Cote, P. Gareil, *Rsc Adv* **2015**, *5*, 64119–64124.
- [20] a) A. Navrotsky, *Phys. Chem. Miner.* **1997**, *24*, 222–241; b) A. Navrotsky, *MRS Bull.* **1997**, *22*, 35–41.

Submitted: May 9, 2016

Accepted: May 24, 2016