

## Uranium Compounds

A Mixed-Valent Uranium Phosphonate Framework Containing U<sup>IV</sup>, U<sup>V</sup>, and U<sup>VI</sup>Lanhua Chen,<sup>[a, b]</sup> Tao Zheng,<sup>[a, b]</sup> Songsong Bao,<sup>[c]</sup> Linjuan Zhang,<sup>[d]</sup> Hsin-Kuan Liu,<sup>[e]</sup> Limin Zheng,<sup>[c]</sup> Jianqiang Wang,<sup>[d]</sup> Yaxing Wang,<sup>[a, b]</sup> Juan Diwu,<sup>\*[a, b]</sup> Zhifang Chai,<sup>[a, b]</sup> Thomas E. Albrecht-Schmitt,<sup>[f]</sup> and Shuao Wang<sup>\*[a, b]</sup>

**Abstract:** It is shown that U<sup>VO</sup><sub>2</sub><sup>+</sup> ions can reside at U<sup>VI</sup>O<sub>2</sub><sup>2+</sup> lattice sites during mild reduction and crystallization process under solvothermal conditions, yielding a complicated and rare mixed-valent uranium phosphonate compound that simultaneously contains U<sup>IV</sup>, U<sup>V</sup>, and U<sup>VI</sup>. The presence of uranium with three oxidation states was confirmed by various characterization techniques, including X-ray crystallography, X-ray photoelectron, electron paramagnetic resonance, FTIR, UV/Vis-NIR absorption, and synchrotron radiation X-ray absorption spectroscopy, and magnetism measurements.

Research regarding the highly soluble and biologically available UO<sub>2</sub><sup>+</sup> unit is not only important for predicting the environmental fate of the highly radiotoxic AnO<sub>2</sub><sup>+</sup> (An=Np, Pu) species<sup>[1]</sup> and the development of remediation strategies,<sup>[2]</sup> but also highly relevant to the design of novel photocatalysts and efficient electrical storage systems based on the reversible electron-transfer couple of UO<sub>2</sub><sup>2+</sup>/UO<sub>2</sub><sup>+</sup>.<sup>[3]</sup> However, the rational synthesis of U<sup>V</sup> crystalline compounds is challenging and

hinders the understanding of the chemistry of the UO<sub>2</sub><sup>+</sup> unit, limited primarily by its inherent instability toward either being disproportionated to U<sup>IV</sup> and U<sup>VI</sup> or oxidized to U<sup>VI</sup>.<sup>[4]</sup> In fact, there is only one natural mineral (wyartite) that contains uranium(V), which highlights the rareness of U<sup>V</sup> in the environment.<sup>[5]</sup> Although organometallic synthesis and high-temperature, high-pressure reactions could yield uranium compounds containing uranium(V),<sup>[6,7c-j]</sup> it is still challenging under mild solvothermal conditions.<sup>[7a,b]</sup>

Owing to the strong affinity of phosphonate ligand toward tetra- and hexavalent actinides, it is even harder to synthesize pentavalent actinide phosphonate, and none has been reported up to date.<sup>[8,9]</sup> This is not surprising because hard donor ligands bind strongly to metal cations with high charge density, leading to elevated preference of disproportionation of pentavalent actinides.<sup>[10]</sup> Herein, by introducing a mild reducing agent methanol into the solvothermal reaction of U<sup>VI</sup> with a diphosphonate ligand (methylenediphosphonic acid, C1P2), [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>1.5</sub>(H<sub>3</sub>O)<sub>1.5</sub>(U<sup>VI</sup>O<sub>2</sub>)<sub>2</sub>(U<sup>V</sup>O<sub>2</sub>)U<sup>IV</sup><sub>2</sub>[CH<sub>2</sub>(PO<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (**1**) was surprisingly obtained as the first phosphonate compound simultaneously containing three oxidation states of uranium (Supporting Information, Figure S1). In comparison, with additional zinc powder, another uranium phosphonate (U<sup>VI</sup>O<sub>2</sub>)<sub>0.5</sub>U<sup>IV</sup>(H<sub>2</sub>O)Zn[CH<sub>2</sub>(PO<sub>3</sub>)<sub>2</sub>][CH<sub>2</sub>(PO<sub>3</sub>)(PO<sub>3</sub>H)] (**2**) could be manually separated as a pure phase of mixed U<sup>IV/VI</sup> complex (Supporting Information, Figure S2).

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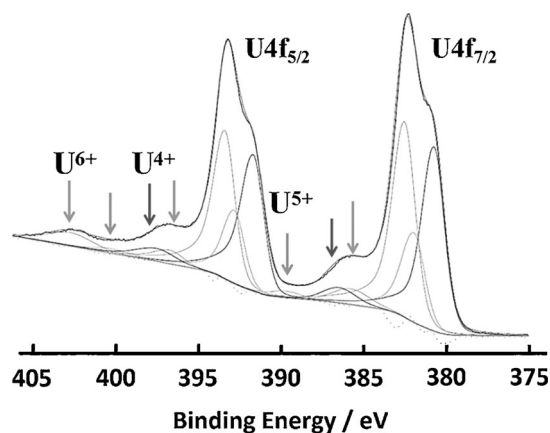
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**Figure 1.** The U 4f XPS spectrum of compound **1**. The spectrum is modeled with three components of U<sup>VI</sup>, U<sup>V</sup>, and U<sup>IV</sup>.

As a powerful technique to identify and quantify oxidation states of uranium,<sup>[11]</sup> X-ray photoelectron spectroscopy (XPS) analysis was first performed on both compounds. As shown in Figure 1, the binding energies (BEs) of the U 4f<sub>7/2</sub> peaks in **1**, as referenced to adventitious C 1s (BE = 285.0 eV), are at 380.75, 381.96, and 382.53 eV, in good agreement with the values for the U<sup>IV</sup> site in [U<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>(L)<sub>6</sub>]·xDMF,<sup>[12]</sup> and the U<sup>VI</sup> site in **2**. Moreover, the BE separations of the satellites from the main peaks are in the typical range of U<sup>IV</sup>, U<sup>V</sup>, and U<sup>VI</sup> components, where the presence of the U<sup>V</sup> is confirmed by the satellite values of 7.75 and 7.44 eV. The XPS data also indicate the presence of U<sup>IV</sup>/U<sup>V</sup>/U<sup>VI</sup> (U 4f<sub>7/2</sub>) with a primary ratio of 2.02:1:2.18 (Supporting Information, Tables S5). Interestingly, for comparison, a decent fitting for the spectrum of **2** could only be achieved using components of U<sup>IV</sup> and U<sup>VI</sup>, where the ratio of U<sup>IV</sup> to U<sup>VI</sup> is 2.02:1 (Supporting Information, Figure S4, Table S6). Furthermore, synchrotron radiation X-ray adsorption near edge structure (XANES) analysis based on the U M<sub>4</sub> edge also supports the presence of U<sup>V</sup> in **1**. Although the absorption peaks of **1** and **2** are both located between those of U<sup>IV</sup> and U<sup>VI</sup> reference samples, the feature of **1** is shifted towards the higher-energy region (Supporting Information, Figure S8, see there also for details).

Compound **1** crystallizes in the P $\bar{1}$  space group and contains three distinct crystallographic sites of uranium (Figure 2a; Supporting Information, Table S2). U(1) and U(2) chains are linked together by C1P2 ligands to form layers, which is further bridged by U(3) into a 3D open-framework structure, as shown in Figure 2a. U(1) is eight-coordinate to form a dodecahedron geometry with U–O bond distances ranging from 2.248(7) to 2.662(7) Å, which shares an edge with the adjacent U(1A) via O(5) and O(5A), resulting in a U<sup>IV</sup> dimer. The bond valence sum

(BVS)<sup>[13]</sup> calculated for this site is 4.03 valence units (v.u.), which is highly consistent with the tetravalent assignment of U(1). U(2) is present in an edge-sharing dimer of pentagonal bipyramidal polyhedra with uranyl U=O distances of 1.776(8) and 1.790(8) Å, respectively, and equatorial U–O distances ranging from 2.271(8) to 2.629(7) Å. The BVS for this site is calculated to be 5.88 v.u. The U(3) site is a tetragonal bipyramid located at the inversion center, with two U=O bond lengths being 1.791(8) Å. Although the uranyl bond distances are within the normal range for U<sup>VI</sup> compounds, the four equatorial U–O bond distances of 2.300(8) Å×2 and 2.308(8) Å×2 are clearly longer than the average distance of ca. 2.25 Å among reported six-coordinated uranyl(VI) compounds, further giving rise to a BVS value of 5.75 v.u., which deviates from the ideal value of 6.<sup>[13b]</sup> Taking the analyses from XPS that show an approximate stoichiometry of U<sup>IV</sup>/U<sup>V</sup>/U<sup>VI</sup> to be 2:1:2 into consideration, it is proposed that such a large amount of U<sup>V</sup> is disorderedly distributed at both U(2) and U(3) sites owing to the structural similarity between U<sup>V</sup> and U<sup>VI</sup> ions. This results in a complex formula of [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>1.5</sub>(H<sub>3</sub>O)<sub>1.5</sub>(U<sup>IV</sup>O)<sub>2</sub>(U<sup>V</sup>O)<sub>2</sub>U<sup>VI</sup>[CH<sub>2</sub>(PO<sub>3</sub>)<sub>2</sub>]<sub>4</sub> for **1**, where hydronium and tetraethylammonium cations exist in the channels to achieve charge neutrality, as suggested by thermogravimetry and differential scanning calorimetry (TG-DSC; Supporting Information, Figure S3), ATR-FT-IR spectra (Supporting Information, Figure S6),<sup>[14]</sup> as well as CHN elemental analysis (Supporting Information, Table S4).

In comparison, the mixed U<sup>IV/VI</sup> compound (U<sup>VI</sup>O)<sub>0.5</sub>U<sup>IV</sup>(H<sub>2</sub>O)Zn[CH<sub>2</sub>(PO<sub>3</sub>)<sub>2</sub>][CH<sub>2</sub>(PO<sub>3</sub>)(PO<sub>3</sub>H)] (**2**) also crystallizes in P $\bar{1}$ , but contains two crystallographically independent uranium sites and the Zn<sup>2+</sup> ion (Figure 2b). Based on the distances of equatorial U–O bonds and two U=O bonds, the BVS values of the uranium centers were calculated to be 5.93 and 4.08 v.u., respectively (Supporting Information, Table S3), which is highly consistent with the XPS analysis.

Moreover, the result of the variable-temperature magnetic susceptibility measurement show that **1** is antiferromagnetically ordered in the low temperature region (Figure 3a).<sup>[15]</sup> Importantly, the data in the high-temperature range from 160 to 270 K can be linearly fitted using the Curie–Weiss law; the corresponding values of *C* and  $\theta$  from the fitting results were calculated to be 5.56 emu K mol<sup>-1</sup> and –840.14 K, respectively, further yielding a  $\mu_{\text{eff}}$  of 2.98  $\mu_{\text{B}}$  per uranium ion. Considering the formula [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>1.5</sub>(H<sub>3</sub>O)<sub>1.5</sub>(U<sup>IV</sup>O)<sub>2</sub>(U<sup>V</sup>O)<sub>2</sub>U<sup>VI</sup>[CH<sub>2</sub>(PO<sub>3</sub>)<sub>2</sub>]<sub>4</sub> proposed from the results of XPS and crystallography analyses, the calculated effective moment is 3.14  $\mu_{\text{B}}$  per U ion using the theoretical values of 3.58  $\mu_{\text{B}}$  and 2.54  $\mu_{\text{B}}$  for U<sup>IV</sup> and U<sup>V</sup> sites based on the Russell–Saunders coupling of the <sup>3</sup>H<sub>4</sub> and <sup>2</sup>F<sub>5/2</sub> ground states, respectively. The slight deviation between the experimental and calculated moments is reasonable, because a reduced moment is often observed for uranium compounds with the effect of crystal field splitting and the antiferromagnetic coupling between the dimers of the U(1) and U(2) centers.<sup>[4,6f,16]</sup> The plot of  $\chi T$  versus *T* presents a similar trend as several reported U<sup>V</sup> compounds (Supporting Information, Figure S9).<sup>[6f]</sup>

Since the pentavalent uranium presents a [Rn]5f<sup>1</sup> electron configuration with Kramers degeneracy, EPR X-band electron

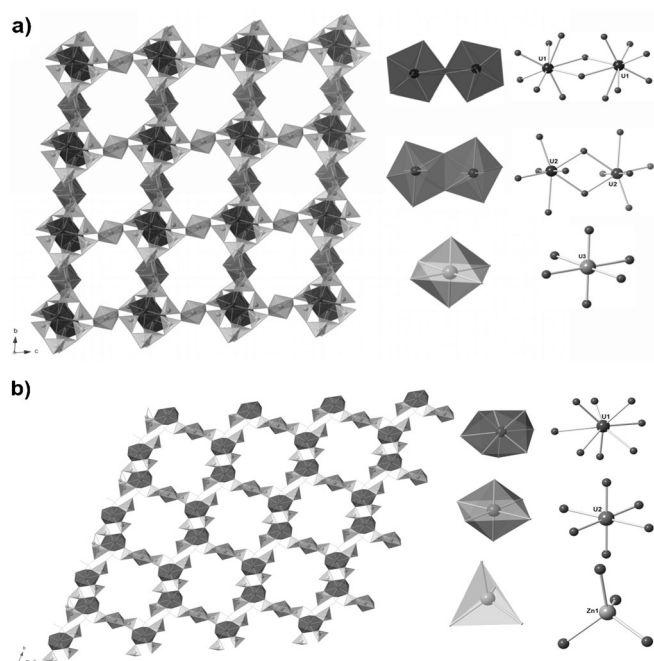
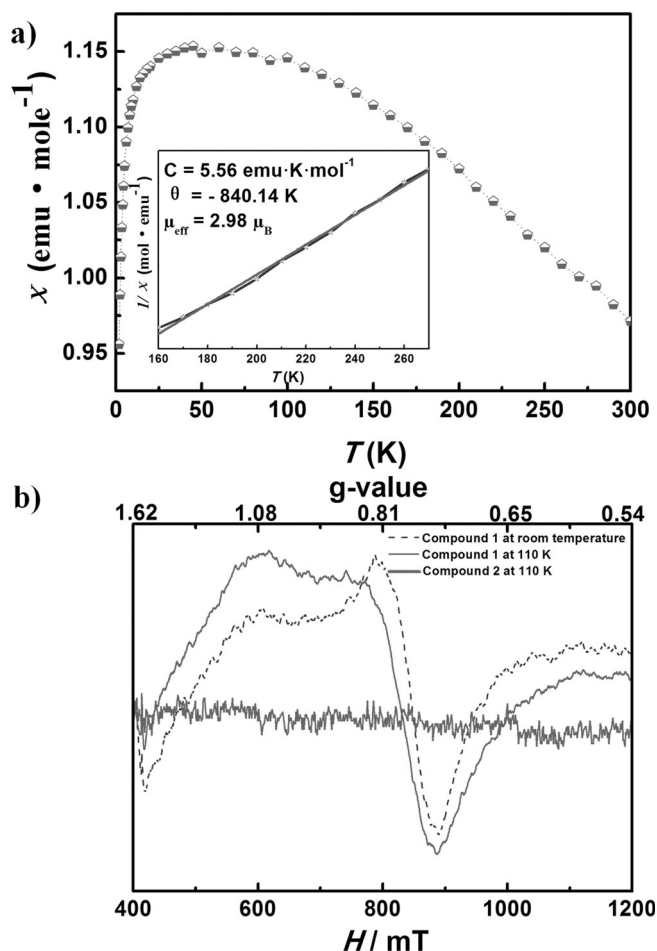


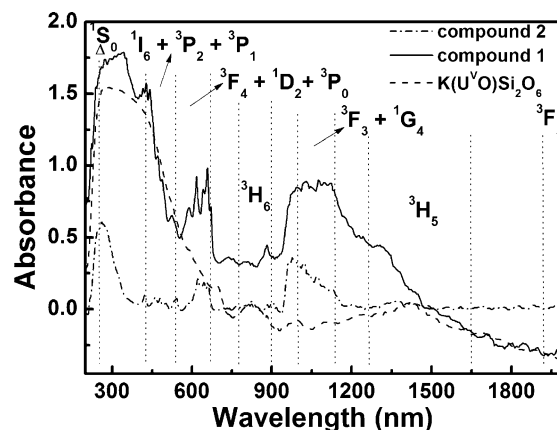
Figure 2. Polyhedral view of compound **1** (a) and **2** (b) along the *a* axis.



**Figure 3.** a) The temperature dependence of magnetic susceptibility of compound 1 measured under an external field of 2000 Oe. Inset: Inverse susceptibility versus temperature plot with a fit using the Curie–Weiss law. b) The X-band EPR spectra of compound 1 and 2 recorded at 110 K.

paramagnetic resonance (EPR) spectra signals can often be captured. Compound 1 presents a clear signal at 856 mT and 837 mT, and the corresponding *g* values are 0.76 and 0.78 at room temperature and 110 K, respectively, whereas compound 2 does not present any intrinsic signal in the range of 400–1200 mT (Figure 3b). The (*g*<sub>⊥</sub>, *g*<sub>∥</sub>) values of 1 are (0.714, 1.220) at room temperature, and (0.710, 1.223) at 110 K, respectively. In comparison, the reported (*g*<sub>⊥</sub>, *g*<sub>∥</sub>) values obtained at room temperature for two U<sup>V</sup> germinates<sup>[7f]</sup> are (0.683, 0.846) and (0.560, 1.254), respectively, and (0.685, 0.773) for U<sup>V</sup>-doped LiTaO<sub>3</sub> powders,<sup>[17]</sup> which are all within the range of 0.56–1.25 for *g* values measured at liquid helium temperature.<sup>[18]</sup> Thus, the EPR results further corroborate the existence of U<sup>V</sup> species in 1. More importantly, this signal did not diminish after exposure to air for at least two months, indicating that U<sup>V</sup> is stable in long terms and protected from the disproportionation.

U<sup>V</sup> could be also identified in the ATR-FT-IR spectrum, where the 770 cm<sup>-1</sup> peak should be ascribed to the asymmetric stretching vibration of the UO<sub>2</sub><sup>+</sup> cation in 1 (Supporting Information, Figure S6). A comparison of the UV/Vis-NIR absorption/diffuse reflectance spectra collected using single crystals of the two compounds and the U<sup>V</sup> reference K(U<sup>V</sup>O)Si<sub>2</sub>O<sub>6</sub><sup>[7g]</sup> evidential-



**Figure 4.** The UV/Vis-NIR absorption spectra of compound 1, 2, and K(U<sup>V</sup>O)Si<sub>2</sub>O<sub>6</sub>.<sup>[7g]</sup>

ly supports the presence of the U<sup>V</sup> component in 1. As shown in Figure 4 and the Supporting Information, Figure S5, a broad charge-transfer peak from 200 nm to 400 nm was observed for 1, contrasting sharply to that of 2, where a relatively narrow peak was observed in this region. Such charge-transfer features originated from the O 2p orbital to the U 6d/5f orbitals were initially interpreted in terms of U<sup>VI</sup> compounds; these features become broader in the spectra of several U<sup>V</sup> compounds,<sup>[6b,7c]</sup> as illustrated by the case of K(U<sup>V</sup>O)Si<sub>2</sub>O<sub>6</sub> (Figure 4), as well as those of U<sup>VI</sup> compounds with elongated uranyl bonds caused by cation–cation interactions.<sup>[19]</sup>

In conclusion, a stable mixed-valent uranium compound (1) has been achieved under mild redox-active solvothermal conditions. It was found unambiguously that U<sup>VI</sup> sites provides compatible locations for U<sup>V</sup> in the crystal lattice owing to their virtue of similar coordination chemistry, where U<sup>V</sup> is generally known as the intermediate species during the reduction process from U<sup>VI</sup> to U<sup>V</sup>. With a newly synthesized mixed U<sup>VI/IV</sup> compound (2) here for comparison, a comprehensive characterization was applied for both compounds that leads to an evidential conclusion of the existence of U<sup>V</sup> in 1, resulting in a new and extremely rare example of a compound containing one element in three oxidation states.<sup>[7j,16,20]</sup> Finally, this synthetic route could lead to a new family of pentavalent actinide compounds, which is beneficial for our further understanding on actinides in this oxidation state as they are significantly problematic during nuclear waste partitioning process.

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- [1] a) R. G. Denning, *J. Phys. Chem. A* **2007**, *111*, 4125–4143; b) N. Edelstein, D. Brown, B. Whittake, *Inorg. Chem.* **1974**, *13*, 563–567.
- [2] a) E. S. Ilton, A. Haiduc, C. L. Cahill, A. R. Felmy, *Inorg. Chem.* **2005**, *44*, 2986–2988; b) R. C. Ewing, *Nat. Mater.* **2015**, *14*, 252–257.
- [3] a) K. Shirasaki, T. Yamamura, Y. Shiokawa, *J. Alloys Compd.* **2006**, *408*, 1296–1301; b) A. Bakac, J. H. Espenson, *Inorg. Chem.* **1995**, *34*, 1730–1735.
- [4] a) P. C. Burns, R. J. Finch, *Am. Mineral.* **1999**, *84*, 1456–1460; b) F. C. Hawthorne, R. J. Finch, R. C. Ewing, *Can. Mineral.* **2006**, *44*, 1379–1385.
- [5] a) J. C. Renshaw, L. J. C. Butchins, F. R. Livens, I. May, J. M. Charnock, J. R. Lloyd, *Environ. Sci. Technol.* **2005**, *39*, 5657–5660; b) J. Selbin, J. D. Ortego, *Chem. Rev.* **1969**, *69*, 657–671.
- [6] a) P. L. Arnold, J. B. Love, D. Patel, *Coord. Chem. Rev.* **2009**, *253*, 1973–1978; b) C. R. Graves, J. L. Kiplinger, *Chem. Commun.* **2009**, 3831–3853; c) L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2006**, *128*, 7152–7153; d) L. Chatelain, J. P. S. Walsh, F. Pecaut, J. Pecaut, M. Mazzanti, *Angew. Chem. Int. Ed.* **2014**, *53*, 13434–13438; *Angew. Chem.* **2014**, *126*, 13652–13656; e) V. Mougél, L. Chatelain, J. Pecaut, R. Caciuffo, E. Colineau, J. C. Griveau, M. Mazzanti, *Nat. Chem.* **2012**, *4*, 1011–1017; f) G. Nocton, P. Horeglad, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2008**, *130*, 16633–16645; g) T. W. Hayton, J. M. Boncella, B. L. Scott, P. D. Palmer, E. R. Batista, P. J. Hay, *Science* **2005**, *310*, 1941–1943; h) P. L. Arnold, D. Patel, C. Wilson, J. B. Love, *Nature* **2008**, *451*, 315–317; i) P. L. Arnold, G. M. Jones, S. O. Odoh, G. Schreckenbach, N. Magnani, J. B. Love, *Nat. Chem.* **2012**, *4*, 221–227.
- [7] a) N. Belai, M. Frisch, E. S. Ilton, B. Ravel, C. L. Cahill, *Inorg. Chem.* **2008**, *47*, 10135–10140; b) S. Wu, J. Ling, S. Wang, S. Skanthakumar, L. Soderholm, T. E. Albrecht-Schmitt, E. V. Alekseev, S. V. Krivovichev, W. Depmeier, *Eur. J. Inorg. Chem.* **2009**, 4039–4042; c) J. T. Stritzinger, E. V. Alekseev, M. J. Polinski, J. N. Cross, T. M. Eaton, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2014**, *53*, 5294–5299; d) H. K. Liu, K. H. Lii, *Inorg. Chem.* **2013**, *52*, 9172–9174; e) C. H. Lin, C. S. Chen, A. A. Shiryayev, Y. V. Zubavichus, K. H. Lii, *Inorg. Chem.* **2008**, *47*, 4445–4447; f) Q. B. Nguyen, C. L. Chen, Y. W. Chiang, K. H. Lii, *Inorg. Chem.* **2012**, *51*, 3879–3882; g) C. S. Chen, S. F. Lee, K. H. Lii, *J. Am. Chem. Soc.* **2005**, *127*, 12208–12209; h) C. S. Lee, S. L. Wang, K. H. Lii, *J. Am. Chem. Soc.* **2009**, *131*, 15116–15117; i) Y. C. Chang, W. J. Chang, S. Boudin, K. H. Lii, *Inorg. Chem.* **2013**, *52*, 7230–7235; j) C. S. Lee, C. H. Lin, S. L. Wang, K. H. Lii, *Angew. Chem. Int. Ed.* **2010**, *49*, 4254–4256; *Angew. Chem.* **2010**, *122*, 4350–4352.
- [8] J. Diwu, T. E. Albrecht-Schmitt in *Metal Phosphonates* (Eds.: A. Clearfield, K. Demadis), RSC Publishing, London, **2011**, Chapter 19, 607–631.
- [9] a) J. Diwu, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2012**, *51*, 4432–4434; b) T. Zheng, Y. Gao, L. H. Chen, Z. Y. Liu, J. Diwu, Z. F. Chai, T. E. Albrecht-Schmitt, S. Wang, *Dalton Trans.* **2015**, *44*, 18158–18166; c) T. Zheng, Q. Y. Wu, Y. Gao, D. X. Gui, S. W. Qiu, L. H. Chen, D. P. Sheng, J. Diwu, W. Q. Shi, Z. F. Chai, T. E. Albrecht-Schmitt, S. Wang, *Inorg. Chem.* **2015**, *54*, 3864–3874; d) T. Zheng, Y. Gao, L. H. Chen, J. Diwu, Z. F. Chai, T. E. Albrecht-Schmitt, S. Wang, *Inorg. Chim. Acta* **2015**, *435*, 131–136; e) W. T. Yang, T. G. Parker, Z. M. Sun, *Coord. Chem. Rev.* **2015**, *303*, 86–109.
- [10] a) J. Diwu, S. Wang, Z. Liao, P. C. Burns, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2010**, *49*, 10074–10080; b) T. H. Bray, A.-G. D. Nelson, G. B. Jin, R. G. Haire, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2007**, *46*, 10959–10961.
- [11] E. S. Ilton, P. S. Bagus, *Surf. Interface Anal.* **2011**, *43*, 1549–1560.
- [12] C. Falaise, C. Volkringer, J. F. Vigier, N. Henry, A. Beaurain, T. Loiseau, *Chem. Eur. J.* **2013**, *19*, 5324–5331.
- [13] a) N. E. Brese, M. O’Keeffe, *Acta Crystallogr. B* **1991**, *47*, 192–197; b) P. C. Burns, R. C. Ewing, F. C. Hawthorne, *Can. Mineral.* **1997**, *35*, 1551–1570.
- [14] a) M. J. Polinski, J. N. Cross, E. M. Villa, J. Lin, E. V. Alekseev, W. Depmeier, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2013**, *52*, 8099–8105; b) P. D. Carnegie, B. Bandyopadhyay, M. A. Duncan, *J. Chem. Phys.* **2011**, *134*, 014302.
- [15] a) J. Yeon, M. D. Smith, A. S. Sefat, H. C. zur Loye, *Inorg. Chem.* **2013**, *52*, 2199–2207; b) S. A. Kozimor, B. M. Bartlett, J. D. Rinehart, J. R. Long, *J. Am. Chem. Soc.* **2007**, *129*, 10672–10674.
- [16] S. A. Wang, E. V. Alekseev, J. Ling, S. Skanthakumar, L. Soderholm, W. Depmeier, T. E. Albrecht-Schmitt, *Angew. Chem. Int. Ed.* **2010**, *49*, 1263–1266; *Angew. Chem.* **2010**, *122*, 1285–1288.
- [17] W. B. Lewis, H. G. Hecht, M. P. Eastman, *Inorg. Chem.* **1973**, *12*, 1634–1639.
- [18] a) J. Selbin, H. J. Sherrill, *Inorg. Chem.* **1974**, *13*, 1235–1239; b) P. Rigny, P. Plurien, *J. Phys. Chem. Solids* **1967**, *28*, 2589–2595; c) M. Drifford, P. Rigny, P. Plurien, *Phys. Lett. A* **1968**, *27*, 620–621.
- [19] Z. H. Weng, S. A. Wang, J. Ling, J. M. Morrison, P. C. Burns, *Inorg. Chem.* **2012**, *51*, 7185–7191.
- [20] C. Dendrinou-Samara, C. M. Zaleski, A. Evagorou, J. W. Kampf, V. L. Pecoraro, D. P. Kessissoglou, *Chem. Commun.* **2003**, 2668–2669.

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