HIP to be Square: Simplifying Nitridophosphate Synthesis in a Hot Isostatic Press

Sebastian Wendl, Sara Mardazad, Philipp Strobel, Peter J. Schmidt, and Wolfgang Schnick*

Abstract: *(Oxo)Nitridophosphates have recently been identified as a promising compound class for application in the field of solid-state lighting. Especially, the latest medium-pressure syntheses under ammonothermal conditions draw attention of the semiconductor and lighting industry on nitridophosphates. In this contribution, we introduce hot isostatic presses as a new type of medium-pressure synthetic tool, further simplifying nitridophosphate synthesis. In a second step, phosphorus nitride was replaced as starting material by red phosphorus, enabling the synthesis of Ca_2PN_3 as model compound, starting only from readily available compounds. Moreover, first luminescence investigations on Eu^{2+}-doped samples reveal $Ca_2PN_3{:}Eu^{2+}$ as a promising broad-band red-emitter ($\lambda_{em} = 650$ nm; fwhm = 1972 cm^{-1}). Besides simple handling, the presented synthetic method offers access to large sample volumes, and the underlying reaction conditions facilitate single-crystal growth, required for excellent optical properties.*

By now, (oxo/imido)nitridophosphates have evolved to one of the best known nitride-based compound classes.[1] The preparation of nitridophosphates, however, has ever been a challenging issue. Initially, using ambient and medium-pressure methods (i.e. (pressure-)ampoules and autoclaves), research on nitridophosphates was significantly accelerated within the last decade by employing high-pressure high-temperature (HP/HT) methods (e.g., multianvil technique).[1–12]

The reason for application of high pressure is that the specially prepared and most commonly used starting material P_3N_5 is thermally not very stable. Therefore, reactions under ambient and medium pressure have to be carried out under gentle conditions, meaning low temperatures ($T > 850$°C; decomposition temperature of P_3N_5) and extraordinary long-term reactions (up to several weeks). According to Le

Chatelier's principle, reactions can be performed much faster under HP/HT conditions, because high pressures prevent thermal decomposition of phosphorus nitride and high-temperature conditions enable reversible cleavage and re-formation of covalent P−N bonds.[13] As reviewed, different synthetic strategies within the high-pressure high-temperature approach could be established, as there are nitride/azide routes, metathesis reactions, Li$_3$N (self-)flux approaches, and the use of mineralizers.[1, 14–18] Consequently, the number of nitridophosphates has steadily been increased, and they have been shown to feature an immense structural diversity.[1] Furthermore, investigations on their materials properties revealed intriguing optical and physical properties, such as luminescence or ion conductivity, illustrating the great potential of nitridophosphates for practical applications.[16,19] Therefore, nitridophosphate research diverged into two different fields, recently. On the one hand, fundamental research focuses on chemical and structural aspects using more sophisticated conditions.[18,20,21] Here, one may consider the synthesis of BP$_3$N$_6$ that starts from refractory h-BN and uses in situ generated HCl as mineralizer, as well as the observation of six-fold N-coordinated phosphorus under extreme pressure ($p > 40$ GPa).[18,20,21] On the other hand, the second branch of nitridophosphate research concerns the examination of their optical and physical properties, with a special focus on luminescent materials, for example, AEP$_8$N$_{14}$:Eu^{2+} ($AE =$ Ca, Sr) has recently been proven as promising host material for Eu^{2+} doping.[19] To enable applications on an industrial scale, however, innovative synthetic routes are required, as sufficient sample quantities cannot be provided by established high-pressure techniques. Therefore, an advanced ammonothermal approach using improved autoclave materials was reconsidered, enabling the access to various nitridophosphates in a medium-pressure range and at higher temperatures.[22–25] However, this method is only restrictedly applicable for industrial use due to scaling issues as it requires operations in supercritical ammonia. Thus, the sought-after large-scale access to nitridophosphates remains a stated goal, until now.

In this contribution, we report on the explorative nitridophosphate synthesis in a hot isostatic press (HIP) that is typically used for sintering and annealing processes in ceramics production and powder metallurgy, but is also an established large-scale technique for nitridosilicate synthesis.[26–31] The HIP approach enables fast chemical reactions under elevated nitrogen pressure, which yield large-volume and crystalline sample quantities, representing a milestone in nitridophosphate synthesis. In order to demonstrate the benefits of HIP syntheses, Ca$_2$PN$_3$ serves as model compound in this contribution. Ca$_2$PN$_3$ is a lowly condensed ($\kappa = n$(P)/

[*] S. Wendl, S. Mardazad, Prof. Dr. W. Schnick
Department of Chemistry, University of Munich (LMU)
Butenandtstraße 5–13, 81377 München (Germany)
E-mail: wolfgang.schnick@uni-muenchen.de

Dr. P. Strobel, Dr. P. J. Schmidt
Lumileds Phosphor Center Aachen, Lumileds (Germany) GmbH
Philipsstraße 8, 52068 Aachen (Germany)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
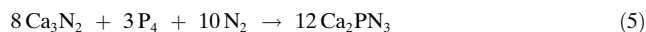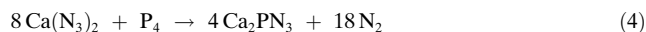https://doi.org/10.1002/anie.202008570.

$n(N) = 1/3$) nitridophosphate, which was initially obtained as microcrystalline powder by reaction of Ca_3N_2 and P_3N_5 in N_2 filled ampoules at 800°C over a period of 14 d [Eq. (1)].[6,7]

$$2 Ca_3N_2 + P_3N_5 \rightarrow 3 Ca_2PN_3 \qquad (1)$$

Employing hot isostatic conditions (150 MPa N_2, 1200°C), this synthesis was initially performed in 10 h (Figures S1 and S2 in the Supporting Information). Subsequently, an alternative protocol starting from $Ca(N_3)_2$ was established [Eq. (2)].

$$6 Ca(N_3)_2 + P_3N_5 \rightarrow 3 Ca_2PN_3 + 16 N_2 \qquad (2)$$
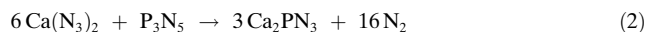
As a third approach, P_3N_5 was replaced by red phosphorus P_{red} as an alternative starting material for further simplification, as shown for ammonothermal synthesis of Ca_2PN_3.[22] Until now, P_{red} could only be used for synthesis of nitridophosphates in combination with (supercritical) ammonia, forming intermediates like "$P(NH_2)_5$" and "$NP(NH_2)_2$".[22–24,32] Applying the HIP approach the use of ammonia can be circumvented. Here, P_{red} initially transforms most likely into gaseous/molecular and highly reactive phosphorus P_4 (or P_2) under the given conditions [Eq. (3)], followed by oxidation into the P^V state. Depending on the starting materials, either azide ions or nitrogen itself serve as redox partner [Eqs. (4) and (5)]. Ca_2PN_3 can thus be synthesized in N_2 atmosphere using only commercially available starting materials, which serves as a far-reaching proof-of-principle for nitridophosphate synthesis in general.

$$4 P_{red} \rightarrow P_4 \qquad (3)$$

$$8 Ca(N_3)_2 + P_4 \rightarrow 4 Ca_2PN_3 + 18 N_2 \qquad (4)$$

$$8 Ca_3N_2 + 3 P_4 + 10 N_2 \rightarrow 12 Ca_2PN_3 \qquad (5)$$

All products of the syntheses above arise as colorless to light beige sinter cakes and are highly sensitive towards air and moisture. For the first time, rod-shaped single crystals ($> 100 \mu m$) of the title compound were obtained (Figure 1).

Therefore, Ca_2PN_3 was for the first time investigated by means of single-crystal X-ray diffraction. Its crystal structure was refined in space group *Cmce* with cell dimension of $a = 5.1987(4)$, $b = 10.3145(10)$ and $c = 11.2834(14)$ Å, which is in good agreement with previous refinements on the basis of powder X-ray diffraction data (Table S1).[6,7,33] A projection of the crystal structure is displayed in Figure 2, and Figure 3 shows the coordination polyhedral of the two crystallographic

Figure 1. SEM images of Ca_2PN_3. Rod-shaped single-crystals $> 100 \mu m$ are observed.
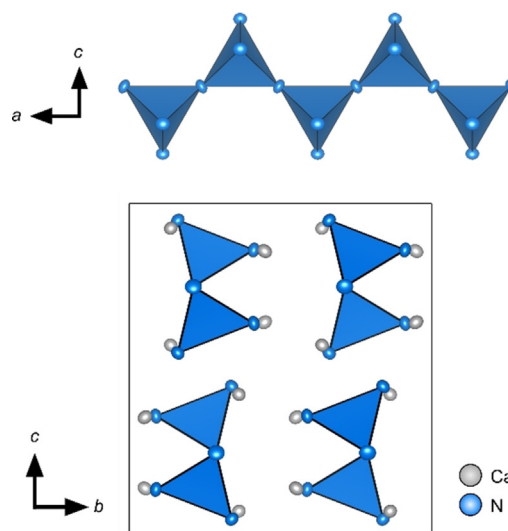

Figure 2. Top: *Zweier* single chains in Ca_2PN_3; bottom: projection of the crystal structure of Ca_2PN_3 along [100]; Ca: gray, N: blue, PN_4 tetrahedra: blue; atoms are displayed with 95% probability.
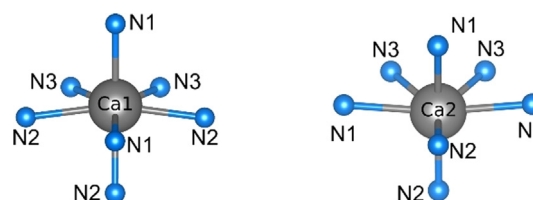

Figure 3. Coordination polyhedra of the two crystallographic Ca^{2+} sites in Ca_2PN_3, as obtained from single-crystal XRD refinement.

Ca sites. A more detailed description of the crystal structure is provided in the literature.[6,7]

The as-refined crystallographic data and a brief comparison to the data provided in literature are given in the Supporting Information (Tables S1–S4).[6,7]

Phase purity of the Ca_2PN_3 samples was confirmed by Rietveld refinement of powder X-ray diffraction data. Although no additional reflections are observed using the obtained structure model from single-crystal X-ray diffraction, significant deviations in intensities arose during Rietveld refinement (Figures S3 and Table S5). This observation is discussed in more detail in the Supporting Information (Figures S4–S6).

The chemical composition was verified by energy dispersive X-ray (EDX) spectroscopy. The averaged stoichiometry $Ca_{1.9(2)}P_{1.0(1)}N_{3.4(3)}$ is in good agreement with the expected sum formula, while trace amounts of oxygen are assigned to surface hydrolysis. Additional traces of chlorine originate from $EuCl_2$ as dopant. The points of measurement and determined values for all elements are documented in the Supporting Information (Figure S7 and Table S6).

In order to investigate luminescence properties of Ca_2PN_3, Eu^{2+}-doped (≈ 3 mol% Eu^{2+} with respect to Ca^{2+}) samples were synthesized using $EuCl_2$ as an additional starting material. The as-obtained samples show deep-red emission ($\lambda_{em} = 650$ nm) upon excitation with blue light ($\lambda_{exc} = 440$ nm, Figure 4). Considering the full width at half maximum (fwhm)
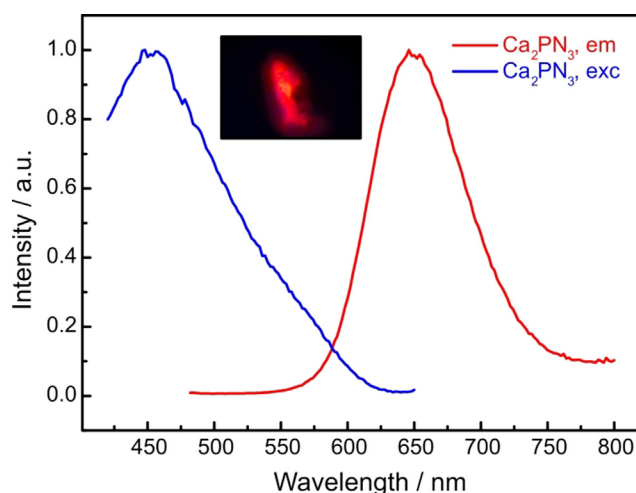
Figure 4. Normalized excitation (blue) and emission spectra (red) of Ca_2PN_3:Eu^{2+}. The small picture section shows a particle of Ca_2PN_3:Eu^{2+} under illumination with UV to blue light.

of 84 nm/1972 cm^{-1} Ca_2PN_3:Eu^{2+} represents the nitridophosphate phosphor with the most narrow red emission band reported so far. Moreover, Ca_2PN_3:Eu^{2+} shows remarkable internal quantum efficiency (IQE) of $\approx 32\%$ for as-synthesized samples. Besides a concentration series for Eu^{2+}-doping in order to increase quantum efficiency, the thermal quenching behaviour could be investigated for potential application.

Such narrow-band red-emitters are still subject of today's research as they are essential to compensate the low sensitivity of the human eye in the near infrared region.[34,35] Avoiding any infrared spillover facilitates high luminous efficacy and allows for a high color rendering index (CRI) and low correlated color temperature (CCT).[34,35] In general, the hitherto obtained results make Ca_2PN_3:Eu^{2+} look competitive in terms of luminescence properties with established red-emitting phosphors from related compound classes, such as $CaAlSiN_3$ (CASN, $\lambda_{em} = 650$ nm, fwhm = 90 nm/2166 cm^{-1}) or $Sr_2Si_5N_8$ (Sr-258, $\lambda_{em} = 630$ nm, fwhm = 85 nm/2150 cm^{-1}), emphasizing the great potential of nitridophosphates. A brief comparison of relevant red-emitting phosphors and their characteristic emission values is provided in Table 1.

Recapitulating, we present a novel synthetic route to nitridophosphates that uses only readily available precursors

and gentle reaction conditions, thus providing industrial scalability of luminescent nitridophosphates for the first time. Especially, the recently introduced PN-based phosphors (e.g.: AEP_8N_{14}:Eu^{2+} or $Ba_3P_5N_{10}Br$:Eu^{2+}) underpin the quest for such an innovative access, as hitherto established methods are sophisticated (supercritical ammonia, specially prepared starting materials), require long reaction times (ampoules, e.g., Ca_2PN_3: 14 d), or provide only insufficient sample quantities (HP/HT). By introducing nitridophosphate synthesis in a hot isostatic press, all above mentioned circumstances can be evaded. Besides easy handling, large-volume samples (>400 mg) can be produced at gentle conditions starting from P_{red} and other commercially available precursors. Thus, the overall duration of nitridophosphate synthesis is speeded up (Ca_2PN_3: 10 h) by hot isostatic pressing. This synthetic tool may considerably accelerate fundamental research on nitridophosphates in particular and on nitridometallates in general. For instance, next to the radically reduced reaction times, fast screenings are enabled, which will facilitate a more thorough characterization of physical properties. Combined with the impressive single-crystal growth, hot isostatic pressing may also simplify structure elucidation of unknown nitride compounds. Accompanied with the possibility of ammonia-free synthesis on a large scale, our work has brought nitridophosphates a step closer to industrial application. In this context, Ca_2PN_3:Eu^{2+} is a promising phosphor and offers numerous possibilities for further investigations of optical properties. Especially, the synthesis of solid solutions $Sr_xCa_{2-x}PN_3$:Eu^{2+} should be in focus, as substitution of Ca^{2+} by larger Sr^{2+} ions may lead to a blue shift of the emission band ending up in the favored emission region between 610 and 620 nm with an even smaller fwhm, avoiding IR spillover. Closing, the synthetic limits of this medium-pressure method should be investigated by the preparation of highly-condensed nitridophosphates.

Conflict of interest

The authors declare no conflict of interest.

Table 1: Comparison of emission properties of Ca_2PN_3:Eu^{2+} with relevant red-emitting Eu^{2+}-doped phosphors.

Compound	λ_{exc} [nm]	λ_{em} [nm]	fwhm [nm]	fwhm [cm^{-1}]
Ca_2PN_3	440	650	84	1972
$Sr_3P_3N_7$[23]	450	681	162	3402
$Sr_2Si_5N_8$[36]	450	630	85	2150
$CaSiN_2$[37]	450	630	110	2790
$CaAlSiN_3$[38,39]	450	650	90	2166
$SrAlSi_4N_7$[40]	450	632	–	2955
$Sr[Mg_3SiN_4]$[41]	450	615	43	1170
$Ba[Mg_3SiN_4]$[42]	450	670	78	1970
$Sr[LiAl_3N_4]$[43]	440	650	50	1180
$Sr[Li_2Al_2O_2N_2]$[44]	460	614	48	1286

[1] S. D. Kloß, W. Schnick, *Angew. Chem. Int. Ed.* **2019**, *58*, 7933–7944; *Angew. Chem.* **2019**, *131*, 8015–8027.

[2] W. Schnick, J. Lücke, *Z. Anorg. Allg. Chem.* **1990**, *588*, 19–25.

[3] W. Schnick, U. Berger, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 830–831; *Angew. Chem.* **1991**, *103*, 857–858.

[4] W. Schnick, J. Lücke, *Z. Anorg. Allg. Chem.* **1992**, *610*, 121–126.

[5] W. Schnick, J. Lücke, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 213–215; *Angew. Chem.* **1992**, *104*, 208–209.

[6] W. Schnick, V. Schultz-Coulon, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 280–281; *Angew. Chem.* **1993**, *105*, 308–309.

[7] V. Schultz-Coulon, W. Schnick, *Z. Anorg. Allg. Chem.* **1997**, *623*, 69–74.

[8] H. Jacobs, F. Golinski, *Z. Anorg. Allg. Chem.* **1994**, *620*, 531–534.

[9] F. Golinski, H. Jacobs, *Z. Anorg. Allg. Chem.* **1995**, *621*, 29–33.

[10] H. Jacobs, R. Nymwegen, *Z. Anorg. Allg. Chem.* **1997**, *623*, 429–433.

[11] H. Jacobs, R. Nymwegen, S. Doyle, T. Wroblewski, W. Kockelmann, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1467–1474.

[12] H. Jacobs, S. Pollok, F. Golinski, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1213–1218.

[13] W. Schnick, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 806–818; *Angew. Chem.* **1993**, *105*, 846–858.

[14] F. J. Pucher, S. R. Römer, F. W. Karau, W. Schnick, *Chem. Eur. J.* **2010**, *16*, 7208–7214.

[15] F. W. Karau, W. Schnick, *J. Solid State Chem.* **2005**, *178*, 135–141.

[16] E.-M. Bertschler, C. Dietrich, J. Janek, W. Schnick, *Chem. Eur. J.* **2017**, *23*, 2185–2191.

[17] S. D. Kloß, W. Schnick, *Angew. Chem. Int. Ed.* **2015**, *54*, 11250–11253; *Angew. Chem.* **2015**, *127*, 11402–11405.

[18] S. Vogel, A. T. Buda, W. Schnick, *Angew. Chem. Int. Ed.* **2018**, *57*, 13202–13205; *Angew. Chem.* **2018**, *130*, 13386–13389.

[19] S. Wendl, L. Eisenburger, P. Strobel, D. Günther, J. P. Wright, P. J. Schmidt, O. Oeckler, W. Schnick, *Chem. Eur. J.* **2020**, *26*, 7292–7298.

[20] S. Vogel, M. Bykov, E. Bykova, S. Wendl, S. D. Kloß, A. Pakhomova, S. Chariton, E. Koemets, N. Dubrovinskaia, L. Dubrovinsky, W. Schnick, *Angew. Chem. Int. Ed.* **2019**, *58*, 9060–9063; *Angew. Chem.* **2019**, *131*, 9158–9161.

[21] S. Vogel, M. Bykov, E. Bykova, S. Wendl, S. D. Kloß, A. Pakhomova, N. Dubrovinskaia, L. Dubrovinsky, W. Schnick, *Angew. Chem. Int. Ed.* **2020**, *59*, 2730–2734; *Angew. Chem.* **2020**, *132*, 2752–2756.

[22] M. Mallmann, S. Wendl, W. Schnick, *Chem. Eur. J.* **2020**, *26*, 2067–2072.

[23] M. Mallmann, S. Wendl, P. Strobel, P. J. Schmidt, W. Schnick, *Chem. Eur. J.* **2020**, *26*, 6257–6263.

[24] S. Wendl, M. Mallmann, P. Strobel, P. J. Schmidt, W. Schnick, *Eur. J. Inorg. Chem.* **2020**, 841–846.

[25] M. Mallmann, C. Maak, R. Niklaus, W. Schnick, *Chem. Eur. J.* **2018**, *24*, 13963–13970.

[26] Z. Xiao, S. Yu, Y. Li, S. Ruan, L. B. Kong, Q. Huang, Z. Huang, K. Zhou, H. Su, Z. Yao, W. Que, Y. Liu, T. Zhang, J. Wang, P. Liu, D. Shen, M. Allix, J. Zhang, D. Tang, *Mater. Sci. Eng. R* **2020**, *139*, 100518.

[27] K. Tsukuma, *J. Ceram. Soc. Jpn.* **2006**, *114*, 802–806.

[28] K. Tsukuma, I. Yamashita, T. Kusunose, *J. Am. Ceram. Soc.* **2008**, *91*, 813–818.

[29] A. G. Padalko, V. A. Baklan, *Inorg. Mater.* **2012**, *48*, 1226–1242.

[30] H. Watanabe, M. Imai, N. Kijima, *J. Am. Ceram. Soc.* **2009**, *92*, 641–648.

[31] H. Watanabe, N. Kijima, *J. Ceram. Soc. Jpn.* **2009**, *117*, 115–119.

[32] J. M. Sullivan, *Inorg. Chem.* **1976**, *15*, 1055–1059.

[33] Crystal data of Ca_2PN_3 from single-crystal XRD refinement: $M = 153.15$ g mol^{-1}, orthothombic, *Cmce* (no. 64), $a = 5.1987(4)$, $b = 10.3145(10)$ and $c = 11.283(1)$ Å, $V = 605.04(11)$ Å^3, $Z = 8$, $\rho = 3.363$ g cm^{-3}, $\mu = 4.031$ mm^{-1}, Mo-K$_\alpha$ ($\lambda = 0.71073$ Å, Bruker D8 Quest), $T = 293$ K, 11 096 observed reflections, 755 independent reflections, 36 parameters, $R_{int} = 0.055$, $R_\sigma = 0.024$, $R1 = 0.017$, $wR2 = 0.043$, $GoF = 1.085$, residual electron density 0.358, -0.603 e Å^{-3}. Deposition Number 2008630 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

[34] C. C. Lin, A. Meijerink, R.-S. Liu, *J. Phys. Chem. Lett.* **2016**, *7*, 495–503.

[35] P. Pust, P. J. Schmidt, W. Schnick, *Nat. Mater.* **2015**, *14*, 454–458.

[36] Y. Q. Li, J. E. J. van Steen, J. W. H. van Krevel, G. Botty, A. C. A. Delsing, F. J. DiSalvo, G. de With, H. T. Hintzen, *J. Alloys Compd.* **2006**, *417*, 273–279.

[37] Y. Q. Li, N. Hirosaki, R.-J. Xie, T. Takada, Y. Yamamoto, M. Mitomo, K. Shioi, *Int. J. Appl. Ceram. Technol.* **2010**, *7*, 787–802.

[38] K. Uheda, N. Hirosaki, Y. Yamamoto, A. Naito, T. Nakajima, H. Yamamoto, *Electrochem. Solid-State Lett.* **2006**, *9*, H22–H25.

[39] H. S. Kim, K.-i. Machida, T. Horikawa, H. Hanzawa, *J. Alloys Compd.* **2015**, *633*, 97–103.

[40] C. Hecht, F. Stadler, P. J. Schmidt, J. Schmedt auf der Günne, V. Baumann, W. Schnick, *Chem. Mater.* **2009**, *21*, 1595–1601.

[41] S. Schmiechen, H. Schneider, P. Wagatha, C. Hecht, P. J. Schmidt, W. Schnick, *Chem. Mater.* **2014**, *26*, 2712–2719.

[42] S. Schmiechen, P. Strobel, C. Hecht, T. Reith, M. Siegert, P. J. Schmidt, P. Huppertz, D. Wiechert, W. Schnick, *Chem. Mater.* **2015**, *27*, 1780–1785.

[43] P. Pust, V. Weiler, C. Hecht, A. Tücks, A. S. Wochnik, A.-K. Henß, D. Wiechert, C. Scheu, P. J. Schmidt, W. Schnick, *Nat. Mater.* **2014**, *13*, 891–896.

[44] G. J. Hoerder, M. Seibald, D. Baumann, T. Schröder, S. Peschke, P. C. Schmid, T. Tyborski, P. Pust, I. Stoll, M. Bergler, C. Patzig, S. Reißaus, M. Krause, L. Berthold, T. Höche, D. Johrendt, H. Huppertz, *Nat. Commun.* **2019**, *10*, 1824.