
This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Mutschke, Alexander; Wylezich, Thomas; Ritter, Clemens; Karttunen, Antti J.; Kunkel, Nathalie

An Unprecedented Fully H—Substituted Phosphate Hydride Sr₅(PO₄)₃H Expanding the Apatite Family

Published in:
European Journal of Inorganic Chemistry

DOI:
[10.1002/ejic.201901151](https://doi.org/10.1002/ejic.201901151)

E-pub ahead of print: 19/11/2019

Document Version
Publisher's PDF, also known as Version of record

Please cite the original version:
Mutschke, A., Wylezich, T., Ritter, C., Karttunen, A. J., & Kunkel, N. (2019). An Unprecedented Fully H⁻-Substituted Phosphate Hydride Sr₅(PO₄)₃H Expanding the Apatite Family. *European Journal of Inorganic Chemistry*, 5073-5076. <https://doi.org/10.1002/ejic.201901151>

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

Apatites

An Unprecedented Fully H⁻-Substituted Phosphate Hydride
Sr₅(PO₄)₃H Expanding the Apatite FamilyAlexander Mutschke,^[a] Thomas Wylezich,^[a] Clemens Ritter,^[b] Antti J. Karttunen,^[c] and
Nathalie Kunkel^{*[a,d]}

Abstract: The apatite family is a mineral class that also contains the biologically very important hydroxyapatite. Here, we are reporting on the synthesis and characterization of a fully hydride-substituted strontium apatite, which could be obtained via mechanochemical synthesis and subsequent annealing treatment. The full substitution by hydride anions is proven by various methods, such as neutron powder diffraction of a deu-

terated sample Sr₅(PO₄)₃D, as well ¹H MAS solid state NMR combined with quantum chemical calculations, vibrational spectroscopy and elemental analysis. The present work expands the apatite family from the known halide and hydroxide apatites to the fully hydride-anion-substituted variant and is expected to open up a new field of materials containing coexistent phosphate and hydride anions.

Replacement and combinations of different anions is known to be a very useful tool in inorganic solid-state materials design.^[1–3] In recent times, especially the search for new mixed-anionic hydrides has become an important research field. For instance, interesting ion conduction and superconducting properties were found in oxide hydrides,^[4,5] and optical properties could be tuned by the combination of hydride with oxides,^[6] fluorides^[7] or even using the newly discovered anion combination of hydride and silicate.^[8] In the present work, we report on an unprecedented fully hydride substituted phosphate hydride Sr₅(PO₄)₃H crystallizing in the known structure of the corresponding fluoride apatite.^[9] While the naturally occurring mineral apatite usually contains halide or hydroxide anions, AE₅(PO₄)₃X with AE = Ca²⁺, Sr²⁺, Ba²⁺ and X = Cl⁻, OH⁻, F⁻, the corresponding fully substituted hydride compounds were not known so far. Recently, Hosono et al. had reported on a phosphate containing hydride anions,^[10] however, in their study the authors found a mixture of hydride and hydroxide anions in the channel sites of the calcium apatite under investigation (estimated maximum hydride occupancy on the corresponding

channel lattice site 0.06). Furthermore, the compound they had obtained showed a green color after UV excitation, which the authors explained by electrons on the X⁻ site. Herein, we show that the coexistence of hydride and phosphate without the presence of further anions such as hydroxide or fluoride can be realized in the apatite structure. The full substitution by hydride anions is shown by neutron powder diffraction of a deuterated sample Sr₅(PO₄)₃D, as well as ¹H MAS solid state NMR combined with quantum chemical calculations, vibrational spectroscopy and elemental analysis.

The hydride apatite Sr₅(PO₄)₃H [Sr₅(PO₄)₃D] was prepared by high-energy ball milling of dried Sr₃(PO₄)₂ with excess of SrH₂ (SrD₂) and subsequent annealing at 500 °C for several days under inert conditions. Sr₅(PO₄)₃H crystallizes hexagonally, similar to its fluoride and hydroxide analogues, in space group P6₃/m (Figure 1). Two unique strontium sites exist. Sr1 is coordinated by 9 O²⁻ anions forming a distorted tricapped trigonal prism (blue); Sr2 comprises of a pentagonal bipyramid with 6 O²⁻ and one H⁻ in its coordination sphere (teal polyhedron, Figure 1c). The crystallographic details can be found in the Table S1 of the Supporting Information.

Due to the low scattering factor of hydride for X-rays and the high incoherent scattering cross section for ¹H for neutrons, neutron powder diffraction data of a deuterated sample were recorded. Figure 2 shows the Rietveld refinement of the structure of Sr₅(PO₄)₃D measured at the high resolution diffractometer D2B at the Institute Laue-Langevin, Grenoble. In order to differentiate between Sr₅(PO₄)₃D and a possible hydroxide apatite Sr₅(PO₄)₃OD, simultaneous refinement of neutron and X-ray diffraction data was performed. As starting models, the structural models of the fluoride and hydroxide analogues were used and cell parameters, atomic positions and shape parameters were refined. As can be expected from the fluoride hydride analogy,^[11] the structures of the hydride and its corresponding fluoride are isotypic. Comparison of the residual values for

[a] Chemistry Department, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany

[b] Institut Laue-Langevin, 71 Rue des Martyrs, 38042 Grenoble, France

[c] Department of Chemistry and Materials Science, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland

[d] Institut für Anorganische Chemie, Universität Göttingen, Tammannstraße 4, 37077 Göttingen, Germany
E-mail: nathalie.kunkel@uni-goettingen.de

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejic.201901151>.

© 2019 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

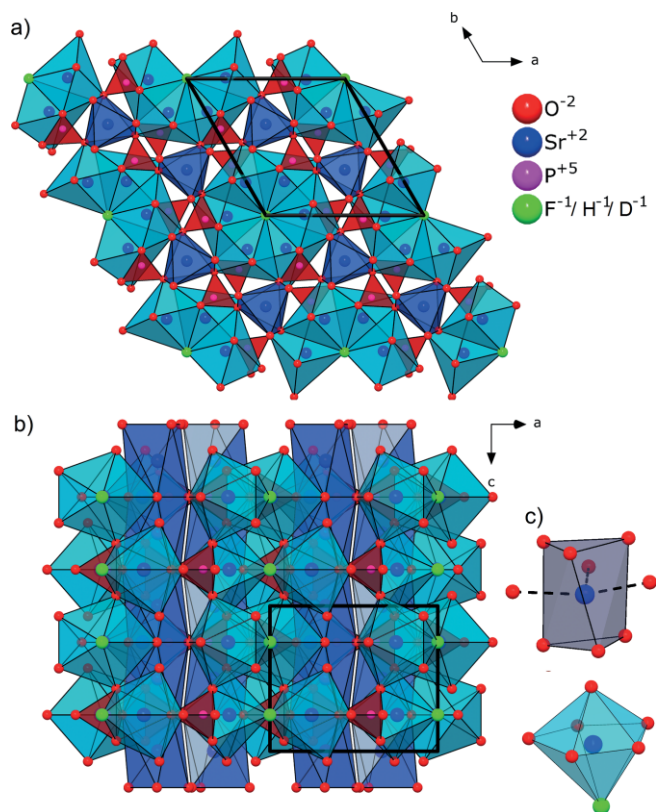


Figure 1. The crystal structure of $\text{Sr}_5(\text{PO}_4)_3\text{F}/\text{H}$. Oxygen atoms are depicted in red, strontium in blue, phosphorus in pink and fluoride/hydride in green. The Sr2 site is surrounded by 6 O^{2-} and one F^-/H^- (teal polyhedra). The Sr1 site (blue polyhedra) has a coordination of 9 O^{2-} anions. Red tetrahedra show $[\text{PO}_4]^{3-}$ units. (a) View along c -axis. While Sr2 polyhedra (teal) are connected via corners, the Sr1 polyhedra (blue) are connected via faces. (b) View along the b -axis. Anions X^- are in a channel along the c -axis. (c) Sr1 (blue polyhedron) and Sr2 (teal polyhedron) with a fluoride/hydride anion in its coordination sphere.

$\text{Sr}_5(\text{PO}_4)_3\text{D}$ and a possible hydroxide $\text{Sr}_5(\text{PO}_4)_3\text{OD}$ favor the model containing exclusively deuteride on the Wyckoff site 2e. As a consequence of the similar ionic radii of hydride and fluoride, the cell parameters derived from X-ray analysis are very close for $\text{X} = \text{H}, \text{D}$ and F . The strontium to deuterium distance is 2.40 Å, which is in the range of known metal hydrides.^[12,13]

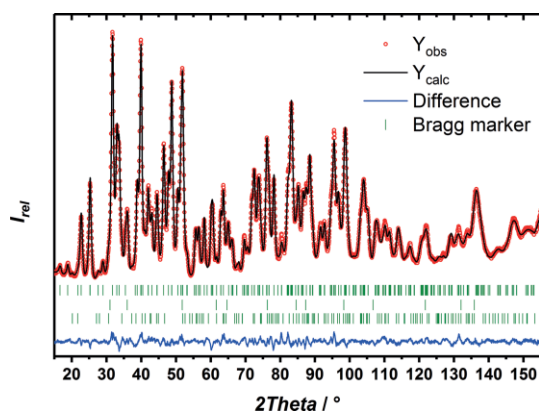


Figure 2. Rietveld refinement of neutron powder diffraction data measured at the D2B diffractometer at ILL Grenoble on $\text{Sr}_5(\text{PO}_4)_3\text{D}$. Bragg markers from top to bottom: $\text{Sr}_5(\text{PO}_4)_3\text{D}$ (85 wt-%), SrO (6 wt-%), $\text{Sr}_3(\text{PO}_4)_2$ (9 wt-%).

To further confirm this assumption, ^1H MAS solid state NMR was carried out. $\text{Sr}_5(\text{PO}_4)_3\text{H}$ shows a chemical shift of 5.48 ppm (see Figure 3), which is comparable with other solid state hydrides as $\text{LiSr}_2\text{SiO}_4\text{D}$ (3.7 ppm),^[8] α/β MgH_2 (ranging from 4.6 to 0.9 ppm)^[14,15] or metal-organic hydride compounds (ranging from 9.9 to 0.5 ppm).^[16,17]

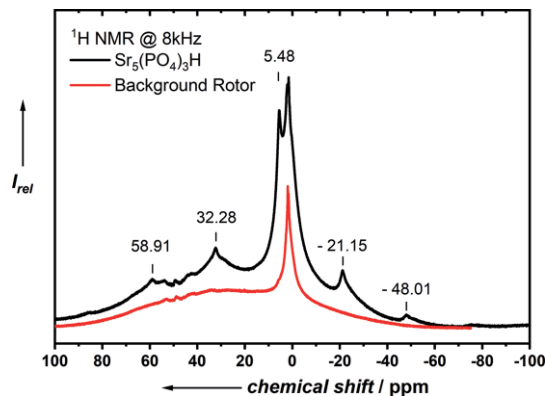


Figure 3. ^1H MAS solid state NMR of $\text{Sr}_5(\text{PO}_4)_3\text{H}$ in a 4 mm ZrO_2 rotor measured on a Bruker AV300. Red curve shows the chemical shift of the blank rotor, which can also be observed in the measurement of the apatite hydride (black curve). $\text{Sr}_5(\text{PO}_4)_3\text{H}$ shows a chemical shift of 5.48 ppm.

Quantum chemical calculations of the solid state ^1H NMR shifts at the DFT-PBE/USPP level of theory^[18] yielded a shift of 5.4 ppm at the experimental geometry of the hydride apatite and 5.3 ppm at the geometry optimized at the same level. These calculated values are in very good agreement with our experimental value of 5.48 ppm. Furthermore, we compared the ^1H MAS solid state NMR spectra of hydroxide $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ with that of our hydride apatite samples in order to confirm the absence of hydroxide anions. In $\text{Sr}_5(\text{PO}_4)_3\text{OH}$, the ^1H atom of the OH^- group exhibits a chemical shift of -0.40 ppm (see Figure S4 SI), which is in the typical range of chemical shifts found for hydroxyl groups in the apatite structure^[19,20] and significantly differs from the values found for the hydride apatite.

Ultimately, we confirmed the absence of OH^- in $\text{Sr}_5(\text{PO}_4)_3\text{H}$ with FTIR spectroscopy, which allows to unambiguously distinguish possible signals of hydroxyl groups. In Figure 4, Figure S3, and Table 1 a comparison of the vibrational spectra of $\text{Sr}_5(\text{PO}_4)_3\text{H}$ and $\text{Sr}_5(\text{PO}_4)_3\text{OH}$ is shown.

In the range between 1100 and 950 cm^{-1} and at approximately 580 cm^{-1} the vibrations of the phosphate host appear (ν_3 , ν_1 and ν_4) for both the hydroxide and the hydride apatite. At approximately 970 cm^{-1} a new broad vibration can be noticed in the hydride apatite. This vibration corresponds to a Sr–H stretching mode according to quantum chemical calculations (see Figure S5 and Table S3 in SI). In good agreement with neutron diffraction and solid state MAS NMR data, no hydroxyl vibration can be found in the FTIR spectra of the hydride apatite $\text{Sr}_5(\text{PO}_4)_3\text{H}$. The characteristic vibration band of the hydroxyl group found in the hydroxide apatite^[21] at 535 cm^{-1} and the stretching band at 3597 cm^{-1} (see Figure S3 SI) are absent in the hydride sample. To the best of our knowledge, these results confirm the successful synthesis of a pure hydride phosphate for the first time.

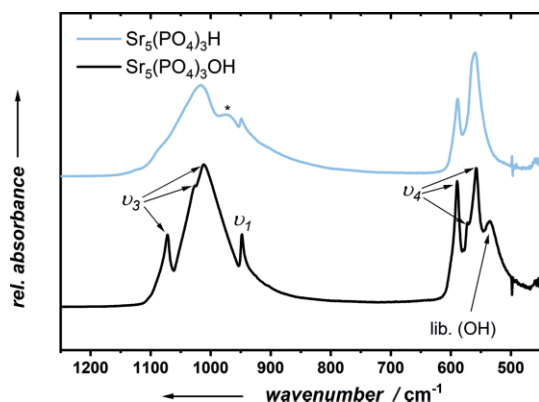


Figure 4. FTIR spectrum of $\text{Sr}_5(\text{PO}_4)_3\text{H}$ and $\text{Sr}_5(\text{PO}_4)_3\text{OH}$. The missing libration vibration (OH) at 535 cm^{-1} and the stretching vibration at 3597 cm^{-1} (OH) (see supporting info Figure S4) in the hydride apatite unambiguously confirm the absence of hydroxide in $\text{Sr}_5(\text{PO}_4)_3\text{H}$. The vibrations ν_1 , ν_3 and ν_4 originate from the phosphate groups. In $\text{Sr}_5(\text{PO}_4)_3\text{H}$ the vibration marked with the star results from the Sr–H stretching mode.

Table 1. Vibrational analysis of the hydroxyl and the hydride apatite. The characteristic vibrations of hydroxyl groups are not present in $\text{Sr}_5(\text{PO}_4)_3\text{H}$.

	vib. (OH)	ν_4	ν_1	ν_3	Stretching vib. (OH)	Stretching vib. (M–H)
$\text{Sr}_5(\text{PO}_4)_3\text{OH}$	535	559, 571, 589	948	1007, 1027, 1072	3597	–
$\text{Sr}_5(\text{PO}_4)_3\text{H}$	–	559, 571, 589	948	1012, 1027, 1085	–	970

In summary, we report on the novel phosphate hydride $\text{Sr}_5(\text{PO}_4)_3\text{H}$, which represents, to the best of our knowledge, the first hydride phosphate containing solely hydride and phosphate anions as well as the first fully hydride substituted apatite. These results were confirmed by several independent methods, such as a neutron powder diffraction, solid state ^1H MAS NMR, quantum chemical calculations, vibrational spectroscopy and elemental analysis. As a consequence, the family of the naturally occurring mineral apatite with the sum formula $\text{AE}_5(\text{PO}_4)_3\text{X}$ with $\text{AE} = \text{Ca}^{2+}$, Sr^{2+} , Ba^{2+} and $\text{X} = \text{Cl}^-$, OH^- , F^- can now be extended to fully substituted hydride apatites. This finding can be expected to open up a new field of materials containing coexistent phosphate and hydride anions, which had, so far, not been known. For instance, hydride phosphates could serve as host materials for optical applications as already suggested for other mixed-anionic hydrides, e.g. temperature sensing^[6–8,22] or possibly as catalysts like the corresponding fluorides.^[23]

Experimental Section

Synthesis of $\text{Sr}_5(\text{PO}_4)_3\text{H}$: A mixture of $\text{Sr}_3(\text{PO}_4)_2$ and SrH_2 (100 % excess) is reacted mechanochemically in a Fritsch Pulverisette 7 Premium Line and a ZrO_2 grinding bowl with 10 ZrO_2 balls (10 mm diameter) at a speed of 650 rpm for 60 cycles under argon atmosphere. One cycle consists of 2 min of milling time and 3 min pauses to reduce heating of the sample. To improve crystallinity the milled sample is pressed to a pellet and heated in an evacuated glass ampoule to $500\text{ }^\circ\text{C}$ for 10 days. Deuterated samples of $\text{Sr}_5(\text{PO}_4)_3\text{D}$

are synthesized via SrD_2 and follow the same procedure as for the hydride.

X-ray diffraction data were collected on a Stoe StadiP diffractometer with transmission geometry, $\text{Cu-K}\alpha_1$ radiation and a solid state detector (Mythen 1K). The samples are placed between two Kapton foils and grease in flat sample holders.

Neutron diffraction experiments were conducted on the high-resolution two-axis diffractometer D2B at the Institute Laue-Langevin, Grenoble with a wavelength of 1.594 \AA . Samples were enclosed air-tight in 8 mm vanadium cylinders. Joint Rietveld refinement of X-ray and neutron diffraction data was carried out using the FullProf program package.^[24] Cell parameters, profile and shape parameters as well as asymmetry functions have been refined. For the structural data in Table S1, the ideal composition $\text{Sr}_5(\text{PO}_4)_3\text{D}$ has been assumed.

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD 1940200.

^1H MAS solid state NMR was carried out on a 300 MHz Bruker AV300 solid state NMR in 4 mm ZrO_2 rotors and a spinning speed of 8 kHz.

Quantum chemical calculations: The solid-state ^1H NMR shifts were calculated with the DFT-PBE method using the CASTEP program package and the GIPAW formalism as implemented in CASTEP-NMR. The IR spectrum of $\text{Sr}_5(\text{PO}_4)_3\text{H}$ was calculated at the DFT-PBE0/TZVP level of theory with the CRYSTAL program package. Full computational details are given in the SI.

FT-IR spectra were recorded on a Spectrum Two (UATR TWO, Perkin Elmer) spectrometer with a diamond sensor. To avoid water and oxygen contamination the device is operated inside an argon filled glovebox. Measurements are taken between 4000 and 500 cm^{-1} with a spectral resolution of 1 cm^{-1} .

Elemental analysis has been conducted on a Vario El microanalyzer and hydrogen content was found to be 0.14 wt.-%, which is in agreement with the calculated value.

Supporting Information (see footnote on the first page of this article): Structural data, IR spectra, quantum chemical calculations.

Acknowledgments

The authors thank Dr. G. Raudaschl-Sieber for ^1H NMR solid state measurements, J. Sicklinger for FTIR measurements, U. Ammari for elemental analysis, and T. F. Fässler for hosting our group. The authors would also like to acknowledge ILL for beam time allocation under the experiment code EASY-399. Data are available from ILL at DOI:10.5291/ILL-DATA.EASY-399. This research received funding from the Deutsche Forschungsgemeinschaft DFG (KU 3427/4-1) and the Fonds der Chemischen Industrie (Li 197/02). A. J. K. thanks Academy of Finland for funding (grant no. 324973) and CSC, the Finnish IT Center for Science, for computational resources.

Keywords: Mixed anionic compounds · Strontium · Hydrides · Apatites · Mechanochemical synthesis · Neutron diffraction

- [1] M. Zeuner, S. Pagano, W. Schnick, *Angew. Chem. Int. Ed.* **2011**, *50*, 7754–7775; *Angew. Chem.* **2011**, *123*, 7898.
- [2] D. Dutzler, M. Seibald, D. Baumann, F. Ruegenberg, H. Huppertz, *Eur. J. Inorg. Chem.* **2019**, 2958–2963.
- [3] S. Schönegger, S. G. Jantz, A. Saxe, L. Bayrjargal, B. Winkler, F. Pielhöfer, H. A. Höpfe, H. Huppertz, *Chem. Eur. J.* **2018**, *24*, 16036–16043.
- [4] G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka, R. Kanno, *Science* **2016**, *351*, 1314–1317.
- [5] S. Iimura, S. Matsuishi, H. Sato, T. Hanna, Y. Muraba, S. W. Kim, J. E. Kim, M. Takata, H. Hosono, *Nat. Commun.* **2012**, *3*, 943, pp. 1–6.
- [6] J. Ueda, S. Matsuishi, T. Tokunaga, S. Tanabe, *J. Mater. Chem. C* **2018**, *6*, 7541–7548.
- [7] T. Wylezich, S. Welinski, M. Hoelzel, P. Goldner, N. Kunkel, *J. Mater. Chem. C* **2018**, *6*, 13006–13012.
- [8] F. Gehlhaar, R. Finger, N. Zapp, M. Bertmer, H. Kohlmann, *Inorg. Chem.* **2018**, *57*, 11851–11854.
- [9] D. A. Grisafe, F. A. Hummel, *J. Solid State Chem.* **1970**, *2*, 160–166.
- [10] K. Hayashi, H. Hosono, *Phys. Chem. Chem. Phys.* **2016**, *18*, 8186–8195.
- [11] A. J. Maeland, W. D. Lahar, *Z. Phys. Chem.* **1993**, *179*, 181–185.
- [12] T. Wylezich, R. Boettcher, A. D. Sontakke, V. Castaing, B. Viana, A. Poepl, N. Kunkel, *J. Phys. Chem. C* **2019**, *123*, 5031–5041.
- [13] a) Yvon, K. and Renaudin, G. (2006). Hydrides: Solid State Transition Metal Complexes. In *Encyclopedia of Inorganic Chemistry* (eds R.B. King, R.H. Crabtree, C.M. Lukehart, D.A. Atwood and R.A. Scott). John Wiley & Sons, Ltd.) b) H. Kohlmann, F. Gingl, T. Hansen, K. Yvon, *Angew. Chem. Int. Ed.* **1999**, *38*, 2029–2032; *Angew. Chem.* **1999**, *111*, 2145.
- [14] P. C. M. M. Magusin, W. P. Kalisvaart, P. H. L. Notten, R. A. van Santen, *Chem. Phys. Lett.* **2008**, *456*, 55–58.
- [15] S. Hayashi, *J. Alloys Compd.* **1997**, *248*, 66–69.
- [16] M. Wiesinger, B. Maitland, C. Färber, G. Ballmann, C. Fischer, H. Elsen, S. Harder, *Angew. Chem. Int. Ed.* **2017**, *56*, 16654–16659; *Angew. Chem.* **2017**, *129*, 16881.
- [17] B. Maitland, M. Wiesinger, J. Langer, G. Ballmann, J. Pahl, H. Elsen, C. Färber, S. Harder, *Angew. Chem. Int. Ed.* **2017**, *56*, 11880–11884; *Angew. Chem.* **2017**, *129*, 12042.
- [18] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [19] P. Hartmann, C. Jäger, S. Barth, J. Vogel, K. Meyer, *J. Solid State Chem.* **2001**, *160*, 460–468.
- [20] R. N. Panda, M. F. Hsieh, R. J. Chung, T. S. Chin, *J. Phys. Chem. Solids* **2003**, *64*, 193–199.
- [21] H. Yu, H. Zhang, X. Wang, Z. Gu, X. Li, F. Deng, *J. Phys. Chem. Solids* **2007**, *68*, 1863–1871.
- [22] T. Wylezich, A. D. Sontakke, V. Castaing, M. Suta, B. Viana, A. Meijerink, N. Kunkel, *Chem. Mater.* **2019**, *31*, 8957–8968.
- [23] S. Sebt, R. Nazih, R. Tahir, L. Salhi, A. Saber, *Appl. Catal. A* **2000**, *197*, L187–L190.
- [24] J. Rodriguez-Carvajal, *Physica B* **1993**, *192*, 55.

Received: October 23, 2019