High-Pressure Chemistry

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Post-Synthetic Modification: Systematic Study on a Simple Access to Nitridophosphates

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Abstract: *Nitridophosphates are a well-studied class of nitrides with diverse materials properties, such as luminescence or ion conductivity. Despite the growing interest in this compound class, their synthesis mostly works through direct combination of starting materials. Herein, we present a systematic study on a promising method for post-synthetic modification by treating pre-synthesized nitridophosphates with halides under elevated pressures and temperatures. Herein, we focus on the applicability of this approach to P/N compounds with different degrees of condensation. Accordingly,* BaP_2N_4, $Ba_3P_5N_{10}Br$, $SrH_4P_6N_{12}$, CaP_8N_{14}, *and* Ca_2PN_3 *are investigated as model compounds for framework-, layer-, and chain-type nitridophosphates. The formation of structurally related, as well as, completely unrelated compounds, compared to the starting materials, shows the great potential of the approach, which increases the synthetic possibilities for nitridophosphates significantly.*

Over the last years, the research on (oxo/imido)nitridophosphates gained attention due to their structural, optical, and physical properties and the development of new technologies and synthesis strategies.[1,2] Nitridophosphates per se can be compared with the oxosilicate class of compounds, as they form tetrahedra-based structures as well. Already initially used ambient and medium-pressure (MP) methods ((pressure-)ampoules, autoclaves) have enabled the preparation of various (oxo/imido)nitridophosphates, phosphorus nitrides, and related compounds.[1,3–10] The variety of nitridophosphates, which are accessible under MP conditions, has recently been increased by hot isostatic pressing and systematic investigations using high-temperature ammonothermal methods.[2,11–14] Despite these advances in MP synthesis, high-pressure high-temperature (HP/HT) conditions are still most commonly used for nitridophosphate synthesis.[1] As recently reviewed, several synthetic routes have been established within this technique, realizing a great diversity of incorporated electropositive elements in anionic P/N tetrahedra substructures.[1,15–19]

Nevertheless, the above mentioned methods and routes are mostly limited to reactions that reassemble starting materials on a fundamental (i.e. atomic) level by bond cleavage and reformation of anionic network structures with embedded counter ions. Even though these approaches have made nitridophosphates one of the most diverse nitride classes, only a restricted synthesis planning and control is possible. While the degree of condensation (i.e. atomic ratio of P/N) of the desired products might be influenced by varying the composition of starting materials, precise structural details can hardly be predicted or even targeted. In order to increase the influence on structural motifs of products, the development of innovative synthesis strategies is essential. Therefore, especially post-synthetic modification appears as a powerful tool, as already pre-arranged nitridophosphates are typically employed. Such topotactic ion-exchange reactions on nitridophosphates have so far only been reported for the synthesis of sodalite-like $Zn_7[P_{12}N_{24}]Cl_2$ by deprotonating $Zn_5H_4[P_{12}N_{24}]Cl_2$ with $ZnCl_2$.[6,20] Moreover, post-synthetic modification by ion exchange has generally been investigated very sparsely on nitride substance classes, although the huge potential of this approach has been demonstrated for related nitridosilicates.[21–24]

In this contribution we present the first systematic study on the post-synthetic modification of nitridophosphates by ion exchange reactions. But, as preliminary tests have shown, that an analogous approach as used for (nitrido-)silicates cannot be easily transferred to nitridophosphates (Figure S1–S3), we combine ion exchange reactions/salt metathesis with HP/HT and MP methods within this work. In particular, we investigate the reaction of pre-synthesized alkaline earth nitridophosphates, which represent framework- (BaP_2N_4 and $Ba_3P_5N_{10}Br$), layer- ($SrH_4P_6N_{12}$ and CaP_8N_{14}), and chain-type (Ca_2PN_3) structures, with halides of the lighter alkaline earth homologues.[10,16,25–28] During these reactions the more negative formation enthalpies of stable byproducts should generate the necessary driving force (e.g. $\Delta H^0(CaCl_2) < \Delta H^0(MgCl_2)$).[29] Moreover, in accordance to Coulomb's law, smaller cations show stronger interactions with anionic nitridophosphate structures, powering the exchange reactions, as well. In order to ensure complete substitution of the initial cations, a 1.5 equivalent excess of the halide was used. Surplus and in situ formed halides were removed after reaction by washing with de-ionized water, given that products are not sensitive to hydrolysis. Structure analyses were performed by Rietveld refinements and chemical compositions of the reaction products were investigated by energy dispersive X-ray spectroscopy (EDX,

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Table S3). Detailed information on the analyses is provided in the Supporting Information.

First experiments were carried out on BaP_2N_4, as it can be classified as a highly condensed framework like the $AE_2Si_5N_8$ structure, for which the ion exchange reaction has been established.[21–24] Using the multianvil technique (5 GPa, 1000 °C) and aiming for BaP_2N_4-type β-SrP_2N_4, a partial replacement of 2/3 of the Ba atoms could be achieved by reaction with $SrCl_2$, yielding homeotypic, literature-known $BaSr_2P_6N_{12}$ [Eq. (1), Figures 1 and S5, Table S4].[30]

$$3\,BaP_2N_4 + 2\,SrCl_2 \rightarrow BaSr_2P_6N_{12} + 2\,BaCl_2 \tag{1}$$

Changing the excess of halides (up to 3 equivalents) or reaction times (10 to 180 min) did not lead to any other observations.

Further the introduced synthesis strategy was conducted on the zeolite-like framework-type nitridophosphate $Ba_3P_5N_{10}Br$, which was reacted with $SrBr_2$, targeting $Sr_3P_5N_{10}Br$ [Eq. (2)].

$$Ba_3P_5N_{10}Br + 3\,SrBr_2 \rightarrow Sr_3P_5N_{10}Br + 3\,BaBr_2 \tag{2}$$

Desired $Sr_3P_5N_{10}Br$ was not formed during reaction, but $BaSr_2P_6N_{12}$ was yielded as a reaction product (Figures 1 and S6, Table S5). Thus, the partial substitution of Ba with Sr leads to a structural collapse of the zeolite-like framework yielding a denser packed structure with smaller tetrahedra rings (*achter* rings in $Ba_3P_5N_{10}Br$, *siebener* rings in $BaSr_2P_6N_{12}$) and cages. Consequently, the mechanism of this reaction cannot be interpreted as a formal ion exchange. Rather, metathesis reactions can be assumed under the applied conditions, underlining the great potential of this method, as the introduction of smaller cations into rigid networks requires the reconstructive rearrangement of P–N bonds and may therefore lead to new structures, as well.

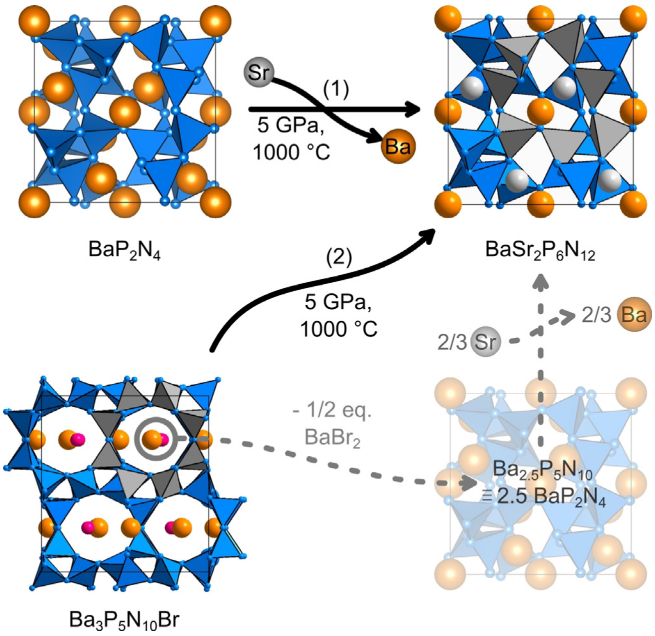

Figure 1. Behavior of BaP_2N_4 and $Ba_3P_5N_{10}Br$ reacting with $SrCl_2$ (route 1) and $SrBr_2$ (route 2), respectively. $BaSr_2P_6N_{12}$ is yielded as product for both reactions. Therefore, BaP_2N_4 may be considered as an intermediate during reaction of $Ba_3P_5N_{10}Br$. Selected *achter* and *siebener* rings in gray, in order to illustrate the structural collapse.[31] Ba in orange, Br in magenta, Sr in gray, PN_4 tetrahedra in blue/gray.

Since both, BaP_2N_4 and $Ba_3P_5N_{10}Br$ transform into $BaSr_2P_6N_{12}$ upon the reaction with $SrCl_2$/$SrBr_2$, one may consider the formation of BaP_2N_4 as an intermediate step during the ion exchange reaction of $Ba_3P_5N_{10}Br$ [Eq. (3) and (4)].

$$Ba_3P_5N_{10}Br \rightarrow Ba_{2.5}P_5N_{10}\ (\equiv\ 2.5\,BaP_2N_4) + 1/2\,BaBr_2 \tag{3}$$

$$3\,BaP_2N_4 + 2\,SrBr_2 \rightarrow BaSr_2P_6N_{12} + 2\,BaBr_2 \tag{4}$$

The potential of post-synthetic modification is further emphasized by its applicability to layered nitridophosphates. For this purpose, $SrH_4P_6N_{12}$ was reacted with $CaCl_2$ under HP/HT conditions [5 GPa, 1000 °C, Eq. (5)].

$$SrH_4P_6N_{12} + CaCl_2 \rightarrow CaH_4P_6N_{12} + SrCl_2 \tag{5}$$

The obtained $CaH_4P_6N_{12}$ shows slight structural changes compared to used $SrH_4P_6N_{12}$ (Figures 2 and S7, Table S6). First, the exchange of Sr with Ca induces a change of the *AE* coordination sphere (SrN_6 prism in $SrH_4P_6N_{12}$, CaN_6 octahedra in $CaH_4P_6N_{12}$). Second, an additional rearrangement of the PN_4 tetrahedra within the layers is observed. Despite these changes, layered nitridophosphates seem basically appropriate for a post-synthetic incorporation of smaller ions, which could to a certain extent be expected given numerous ion exchange experiments on related phyllosilicates and other lamellar clay minerals.[32–34] This might be due to a great tolerance to the ionic radii of counter ions. While the covalent P–N bonds in the tetrahedra layers are rigid, the more ionic *AE*-N contacts are less directional and therefore more flexible. Thus, smaller ionic radii may be countered by decreasing the distances between layers, or a rotation/horizontal shift of the layers, as observed for $CaH_4P_6N_{12}$. Similar translation effects have already been described for silicates, as well.[35] Corresponding investigations on 2D structure types had not been performed on any related nitride compound classes, as yet.

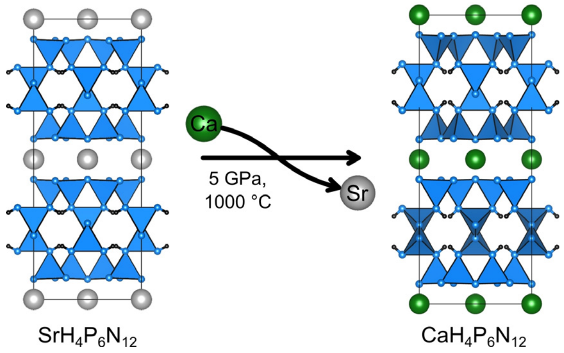

Figure 2. Illustration of the reaction of $SrH_4P_6N_{12}$ with $CaCl_2$, yielding $CaH_4P_6N_{12}$. Sr in gray, Ca in green, H in black, PN_4 tetrahedra in blue.

A second layered nitridophosphate, namely CaP_8N_{14}, which is structurally related to $CaH_4P_6N_{12}$, was reacted with $MgCl_2$ at HP/HT conditions of 5 GPa, 1000 °C resulting in MgP_8N_{14} [Eq. (6), Figure 3].

$$CaP_8N_{14} + MgCl_2 \rightarrow MgP_8N_{14} + CaCl_2 \tag{6}$$

The obtained MgP_8N_{14} has previously not been accessible by conventional synthesis and its structure was now elucidated from powder diffraction data, with a detailed discussion provided in the Supporting Information (Figures S8 and S9, Table S7).[36]

The closely similar structures of AEP_8N_{14} ($AE = \mathrm{Mg, Ca}$) indicate a topotactic reaction, which might be realized through the highly-condensed quadruple layers of CaP_8N_{14} with ($\kappa = 0.57$). Thus, the PN_4 tetrahedra layers are assumed to be rather rigid, while Ca^{2+} ions in between remain mobile and easily accessible.

However, even for this reaction not all aspects suggest an ion-exchange mechanism, according to the common principle. For instance, when comparing the powder X-ray diffraction data of the starting material and the product, it is noticeable that an amorphous portion of the product decreases significantly (Figure S10). Such recrystallization effects indicate increased crystal growth during reaction, which might require reconstructive cleavage and reformation of P–N bonds, as well.

The results described so far suggest that lower dimensional networks are suitable for post-synthetic modification. Therefore, lowly condensed Ca_2PN_3 was examined as a model compound for nitridophosphates with one-dimensional chain structures (Figures 4). In a hot isostatic press, Ca_2PN_3 was reacted at 150 MPa and 1000 °C with $MgCl_2$, following Equation (7), resulting in the formation of Mg_2PN_3 and $CaCl_2$ with MgO as a minor side phase (Figure S11, Table S8).

$$Ca_2PN_3 + 2\,MgCl_2 \rightarrow Mg_2PN_3 + 2\,CaCl_2 \tag{7}$$

In contrast to CaP_8N_{14}, the exchange of Ca by Mg causes structural changes for AE_2PN_3 ($AE = \mathrm{Mg, Ca}$). While the *zweier* single chains are stretched for Ca, they are distorted for Mg_2PN_3 in order to counter the smaller ionic radius. This leads to a change from pentagonal bipyramidal (Ca^{2+}) to tetrahedral coordination (Mg^{2+}) of the *AE* ion.

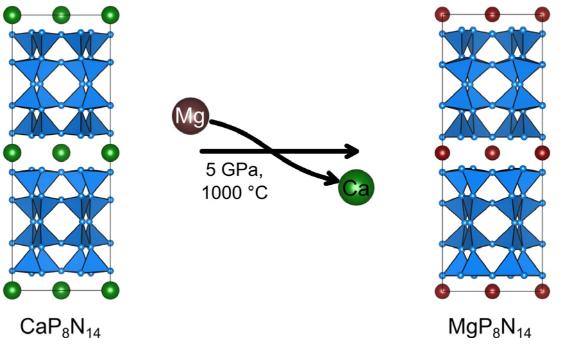

Figure 3. Observed reaction for CaP_8N_{14} with $MgCl_2$. Ca in green, Mg in brown, PN_4 tetrahedra in blue.

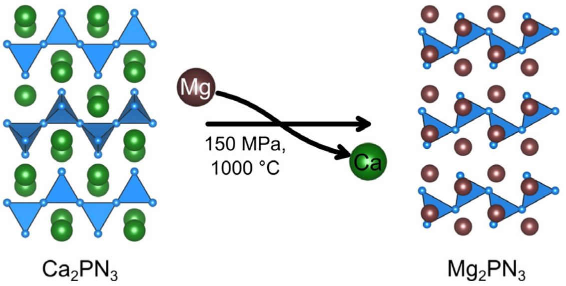

Figure 4. Schematic reaction for Ca_2PN_3 with $MgCl_2$. Ca in green, Mg in brown, PN_4 tetrahedra in blue.

Inspired by the ion exchange on nitridosilicates we have tried to transfer the applied principle to nitridophosphates using MP and HP/HT techniques. Thereby, we found a versatile reaction behavior for nitridophosphates. Apart from homeotypic compounds ($BaSr_2P_6N_{12}$, MgP_8N_{14}), related structures ($CaH_4P_6N_{12}$, Mg_2PN_3) and even completely different structure types ($BaSr_2P_6N_{12}$ starting from $Ba_3P_5N_{10}Br$) can be obtained by the reaction of pre-synthesized nitridophosphates with halides.

Considering possible driving forces of the presented approach, the targeted formation of the more stable halides and Coulomb's law certainly have a major influence. Similar explanations are given for metathesis reactions or a corresponding ion exchange in nitridosilicates.[21–24,37] Furthermore, a possible reduction in volume can be considered as driving force, as MP and HP/HT conditions were applied. However, more precise conclusions about this assumption cannot be drawn, since structural information on all starting materials and products under the experimental reaction conditions would be necessary.

In summary, the reaction behavior of pre-synthesized nitridophosphates, that represent framework-, layer-, and chain-type structures and cover the degree of condensation from $\kappa = 1/3$ to 4/7, was investigated in presence of alkaline earth halides by means of ion exchange under elevated pressures. Within the presented substantial overview a diverse reaction behavior of the starting materials was observed, demonstrating the enormous potential and the broad applicability of this alternative approach. Even if only the three-dimensional structure of $Ba_3P_5N_{10}Br$ has completely collapsed, some of the lower dimensional nitridophosphates show structural changes, as well. Thus, both the simple synthesis of unprecedented isotypic compounds, as well as the synthesis of completely new structure types may be enabled in the future. Therefore, our work can be seen as a far-reaching proof-of-principle that pre-synthesized nitridophosphates can be reacted with halides. However, no trends regarding reaction mechanisms or the accessibility of different structure types can be deduced in the context of this work. At this point, in situ investigations at elevated pressures are essential for a better understanding of these reactions and should be subject to future investigations, as well as the investigation of the reaction behavior of further nitridophosphates towards halides.

Furthermore, the experiments will be expanded to other metal halides, in order to increase the variety of cations (transition, rare-earth, noble metals) in nitridophosphates. Consequently, this post-synthetic strategy could therefore present a breakthrough in the search for a universal access to nitridophosphates with embedded cations of various types.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: high-pressure chemistry · ion exchange · nitrides · nitridophosphates · post-synthetic modification

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