High-Pressure Chemistry

High-Pressure High-TemperatureSynthesis of Mixed Nitridosilicatephosphates and Luminescence of AESiP3N7:Eu2+
(AE = Sr, Ba)

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Dedicated to Professor Thomas M. Klapótke on the occasion of his 60th birthday

Abstract: Tetrahedra-based nitrides with network structures have emerged as versatile materials with a broad spectrum of properties and applications. Both nitridosilicates and nitridophosphates are well-known examples of such nitrides that upon doping with Eu2+ exhibit intriguing luminescence properties, which makes them attractive for applications. Nitridosilicates and nitridophosphates show manifold structural variability; however, no mixed nitridosilicatephosphates except SiPN7 and SiP2N4NH have been described so far. The compounds AESiP3N7 (AE = Sr, Ba) were synthesized by a high-pressure high-temperature approach using the multianvil technique (8 GPa, 1400–1700 °C) starting from the respective alkaline earth azides and the binary nitrides P,Nx and Si,Nx. The latter were activated by NH,F, probably acting as a mineralizing agent. SrSiP3N7 and BaSiP3N7 were obtained as single crystals. They crystallized in the barylite-1O (M = Sr) and barylite-2O structure types (M = Ba), respectively, with P and Si being occupationally disordered. Cation disorder was further supported by solid-state NMR spectroscopy and energy-dispersive X-ray spectroscopy (EDX) mapping of BaSiP3N7 with atomic resolution. Upon doping with Eu2+, both compounds showed blue emission under UV excitation.

Introduction

Emerging environmental consciousness has pushed the development of solid-state lighting solutions forward. The invention of efficient InGaN-based blue LEDs (light-emitting diodes) enabled the development of pc-LEDs (phosphor-converted) with remarkable properties in terms of color temperature, color rendition, and efficacy. Significant improvements in the aforementioned properties were possible due to nitride compounds such as M2Si,Nx:Eu2+ (M = Sr, Ba), MSi2O,Nx:Eu2+ (M = Ca, Sr, Ba), SrLiAl,N3:Eu2+, and MASi,N3:Eu2+.[5-6]

Materials properties concerning solid-state lighting can be tuned by dopant concentration to a limited extent, affecting Stokes shifts in emission spectra, or by a variation of the size of coordination polyhedra by substitution such as introducing Sr on Ba sites. Completely shifted emission properties, however, can only be achieved by a fundamental alteration of the host lattice.[5-6]

The main goal of this work was to expand the compositional and structural diversity of tetrahedra-based luminescent materials. Thus, discovery of the title compounds SrSiP3N7 and BaSiP3N7 opens up the novel compound class of mixed nitridosilicatephosphates, which can now be further explored as innovative host lattices. While nitridosilicates have been investigated thoroughly and nitridophosphates show similar promising structures and properties, only two compounds that contain both Si,Nx (x = 4, 6) and P,Nx units have been reported so far, that is, SiPN4 and SiPN4NH.[7-8] The crystal structure of SiPN4 corresponds to a defect wurtzite-type arrangement with mixed occupation of Si and P at the tetrahedral sites. The crystal structure of SiPN4,NH is related to sillimanite-type Al2SiO5. It is built up from edge-sharing Si,N octahedra interconnected by all-side vertex-sharing PN4 tetrahedra. A possible explanation for the challenges concerning syntheses that are involved in the preparation of mixed nitridosilicatephosphates could be the chemical inertness of Si,Nx while P,N3 already decomposes at temperatures above 850 °C if no external pressure is applied. As shown in previous publications, according to Le Chatelier's...
principle, the decomposition of P₄N₄ under the formation of N₂ is suppressed by external pressure.[10]

NH₄Cl has been successfully employed as a mineralizer facilitating crystal growth of nitridophosphates. HCl formed in situ most likely leads to reversible P–N bond formation and cleavage.[11,12] After nitridosilicatephosphates proved to be not accessible with the help of NH₄Cl, changing the mineralizing agent to NH₄F afforded the title compounds AESP,N₄ (AE=Sr, Ba). This may be explained by the fact that HF cannot only reversibly cleave and form P–N bonds, but also Si–N bonds. The surface of Si,N₄ features SiNH₃ groups that can be attacked by F⁻ in a nucleophilic substitution.[13]

Results and Discussion

The nitridosilicatephosphates AESP,N₄ (AE=Sr, Ba) were synthesized by high-pressure high-temperature (HP/HT) reactions at 8 GPa and 1400 °C (Ba) and 1700 °C (Sr), respectively, using a modified Walker-type multianvil apparatus.[14] The synthesis of SrSiP,N₄ at temperatures below 1700 °C resulted in samples with significant amounts of unknown side phases. Reactions followed the so-called azide route using P,N₃, Si,N₃ and the respective metal azide as starting materials with additional NH₄F (∼5 wt%) as a mineralizing agent (Eq. (1)). To investigate luminescence properties, samples with the addition of approximately 1 mol% of EuF₃ (concerning AE=E⁴⁻) to the starting mixture were prepared.

3 AE (N₃)₃ + 3 P,N₃ + Si,N₃ NH₄F ↔ 3 AESP,N₄ + 8 N₂ (1)

The title compounds were obtained as colorless powders (Eu²⁺-doped samples of SrSiP,N₄ show a yellow tint) and showed no sensitivity to air or moisture. More detailed information on the HP/HT synthesis is given in the Supporting Information.

The crystal structures were elucidated by single-crystal X-ray diffraction (SCXRD) using direct methods and least-squares refinement. SrSiP,N₄ crystallizes in space group Pmn₂ (no. 31) with Z = 2. BaSiP,N₄ crystallizes in space group Pmma (no. 62) with Z = 4; details are given in Tables 1 and S2–7. In addition, Rietveld refinements indicate the presence of BaSiP,N₄ crystallizing in space group Pmn₂ (no. 31) with Z = 2 as a side phase. Both compounds are isotypic to the two polymorphs of barylite BaBeSiO₄. SrSiP,N₄ corresponds to the barylite-10 polymorph, whereas BaSiP,N₄ features the structure of barylite-20. The structures of barylite-10 and barylite-20 represent the maximum degree of order (MDO) polytypes of their polytype family. Both structures consist of a network of all-vertex-sharing PN₄ and (Si₈P₉)₄N tetrahedra and elongated square pyramidal (J₄) AEN₄ (AE=Sr, Ba) polyhedra (Figure S1).[15]

The main difference between the two polymorphs concerns the arrangement of tetrahedra. While in SrSiP,N₄ all tetrahedra vertices point in the same direction, those in BaSiP,N₄ alternate, which results in a doubled unit cell with 2b (SrSiP,N₄) = a (BaSiP,N₄) (Figure 1). Although tetrahedra orientation differs in both compounds, the environment of AE atoms is strikingly similar. The tetrahedra connection patterns show that both compounds consist of dreier, vierer, and sechser rings that, apart from slight distortions, are arranged and distributed in the same manner (Figure 2), leading to the same topology point symbol [3⁺,4⁺,5⁺,6⁺][3⁺,4⁺,5⁺,6⁺].[16] Both compounds exhibit one tetrahedrally coordinated site shared by Si and P, while the other site is solely occupied by P. Further details of the crystal structure investigations may be obtained from the joint CCDC/FIZ Karlsruhe online deposition service by quoting the deposition numbers CSD-2050660 and 2050661. In the case of SrSiP,N₄, potential ordering of Si and P was considered by symmetry reduction and refinement of the structure against SCXRD data in the subgroups P₃, Pn, and Pm of space group Pmn₂. However, no indications of complete ordering were found. In all structure models, the volumes of the resulting four symmetrically independent tetrahedra were compared as (PSi)–N bond lengths were not sufficiently meaningful for discrimination.[17] This investigation led to two different kinds of tetrahedra.

Structure models in subgroups P₃, Pn, and Pm reveal two tetrahedra exhibiting a volume of 22.1–22.4 Å³ that coincides with the volume of PN₄ tetrahedra from known nitridophosphates in literature and corresponds to one site in the final structure model in Pmn₂. The other two tetrahedra have a volume of 23.7–24.0 Å³, which lies between the volumes of PN₄ (21.3–22.8 Å³) and Si₈N₄ tetrahedra (25.2–27.6 Å³) (Tables S10 and 11).[8,9,26–28,16–22] BVS (bond valence sum) calculations performed on all structure models revealed two tetrahedrally occupied sites with tetrahedrally occupied by P and two tetrahedrally occupied by Si and P in a 1:1 ratio (Tables S13–15).[29]

Table 1. Crystallographic data of the single-crystal structure refinements of AESP,N₄ (AE=Sr, Ba). Standard deviations are given in parentheses.

| Formula | SrSiP,N₄ | BaSiP,N₄ |
|---------|----------|----------|
| molar mass (g mol⁻¹) | 306.69 | 356.41 |
| crystal system | orthorhombic | orthorhombic |
| space group | Pmn₂, (no. 31) | Pmma, (no. 62) |
| density (g cm⁻³) | 3.699 | 4.142 |
| formula units/unit cell | 10.807 | 7.927 |
| temperature [K] | 296(2) | 297(2) |
| wR² | 0.0731 | 0.0599 |
| R-values (all data) | R₁ = 0.0343 | R₁ = 0.0340 |
| ρM (Å⁻²) | 2.18, -1.49 | 0.81, -1.53 |
In the case of BaSiP$_3$N$_7$, the ordering of tetrahedra was considered by symmetry reduction and refinement of the structure against SCXRD data in subgroups Pna$_2$1, P$_2$1ma, and P$_2_1$/$c$ of space group Pnma. Only subgroups retaining the extinction condition of the a glide planes present in Pnma were taken into account because electron diffraction parallel to [001] showed no violation of the extinction conditions. Additional electron diffraction patterns parallel to [100] showed no violation of the extinction conditions of the n glide, too, further supporting the structure model in space group Pnma (a comparison of experimental diffraction patterns with simulated ones based on the structure model in space group Pnma is given in Figure S5).

The comparison of resulting tetrahedral volumes showed the same features as for SrSiP$_3$N$_7$ (Table S12). BVS calculations performed for the different structure models again suggested two sites completely occupied by P and two sites shared by Si and P (Tables S16–18). The simple approach of comparing tetrahedra volume as a tool for assigning Si and P, which lack scattering contrast, to the respective sites was indeed confirmed by scanning transmission electron microscope energy-dispersive X-ray spectroscopy (STEM-EDX) mapping with atomic resolution for BaSiP$_3$N$_7$. These data support the model in space group Pnma, showing two sites with mixed Si/P occupation (Figure 3, enlarged version see Figure S6). This result is also corroborated by $^{31}$P solid-state magic angle spinning (MAS)-NMR spectra, which show a broad signal [full width at half-maximum (fwhm) = 19.7 ppm] that is consistent with a dis-
ordered model (Figure 4, Figure S4). Line broadening in the NMR spectrum is probably due to disorder in the second coordination sphere of P atoms. In contrast, ordered nitrides like BP$_3$N$_6$ or Li$_{12}$P$_3$N$_9$ show very narrow signals in their $^{31}$PNMR spectra.\[8, 30\] In both structures, the connectivity of the tetrahedra via their vertices can explain the presence of different tetrahedral volumes. The smaller tetrahedra have three vertices occupied by twofold bridging nitrogen atoms N$_{\text{2}}$ and one vertex occupied by a threefold bridging nitrogen atom N$_{\text{3}}$. Chemical analysis by EDX agrees with the sum formulas. Due to ambiguous O contents (as indicated by EDX measurements) either surface hydrolysis or slight compositional variations cannot completely be ruled out so that a phase width according to AE$_{\text{Si}}$N$_7$O$_x$ (AE = Sr, Ba) with $x < 1$ could also be considered (Table S8) even though some analyses show no O.

Upon doping with Eu$^{2+}$, both compounds emit blue light under UV excitation. Luminescence spectra show emission maxima of $\lambda_{\text{max}} = 430$ nm for SrSiP$_3$N$_7$:Eu$^{2+}$ and $\lambda_{\text{max}} = 424$ nm for BaSiP$_3$N$_7$:Eu$^{2+}$ upon excitation with $\lambda_{\text{exc}} = 400$ nm. The emission curves were extrapolated to give an estimate of the fwhm, which amount to 45 nm (2404 cm$^{-1}$) for SrSiP$_3$N$_7$:Eu$^{2+}$ and 53 nm (2731 cm$^{-1}$) for BaSiP$_3$N$_7$:Eu$^{2+}$ (Figure 5). The corresponding Stokes shifts are 38 nm (2254 cm$^{-1}$) for SrSiP$_3$N$_7$:Eu$^{2+}$ and 32 nm (1925 cm$^{-1}$) for BaSiP$_3$N$_7$:Eu$^{2+}$. The presence of a single narrow emission band for both phosphors can be explained by the emission properties of Eu$^{2+}$ and the presence of a single crystallographic site for the alkaline earth ions suitable for doping with Eu$^{2+}$ with AE–N distances ranging from 2.696(3)–3.270(3) Å (SrSiP$_3$N$_7$) to 2.872(3)–3.230(3) Å (BaSiP$_3$N$_7$). The similarity of emission properties in terms of fwhm are most likely to be explained by the P–Si$_3$P$_{0.5}$ cages around the AE position, which are very similar. Thus, only minute deviations are caused by different AE cation sizes even though both structures differ with respect to their space groups, unit cell volumes, and tetrahedra orientations.

Conclusions

High-pressure high-temperature synthesis with the addition of NH$_4$F is a suitable approach to the synthesis of mixed nitridosilicatephosphates. The compounds AEs$_{1-x}$P$_{x}N_7$O$_x$ (AE = Sr, Ba) adopt the structure types of the two polymorphs of the mineral barylite. This structure type has not been observed for nitride compounds so far. Although silicon and phosphorus exhibit little contrast in X-ray diffraction, the comparison of polyhedra volumes led to structure models with an occupationally disordered site that also persists if potential ordering is considered by symmetry reduction. The disordered model for BaSiP$_3$N$_7$ is further supported by solid-state NMR spectroscopy. Scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDX) mapping with atomic resolution enables to directly observe said disorder, which is additionally in accordance with systematic absences observed in electron dif-
fraction patterns. Therefore, nitridosilicatephosphates have the potential to significantly diversify the structural chemistry of nitrides. Their suitability as host lattices for rare-earth activator ions seems especially intriguing considering the emission properties of other compounds with multiple tetrahedra centers like CaAlSiN$_3$:Eu$^{2+}$, Sr[Li$_2$Al$_2$O$_2$N$_2$]:Eu$^{2+}$, or Sr[LiAl$_2$N$_2$]:Eu$^{2+}$.[2,31,32]

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Conflict of interest

The authors declare no conflict of interest.

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