

## Luminescence | Very Important Paper |

# VIP Nitridophosphate-Based Ultra-Narrow-Band Blue-Emitters: Luminescence Properties of $AEP_8N_{14}:Eu^{2+}$ ( $AE = Ca, Sr, Ba$ )

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**Abstract:** The nitridophosphates  $AEP_8N_{14}$  ( $AE = Ca, Sr, Ba$ ) were synthesized at 4–5 GPa and 1050–1150 °C applying a 1000 t press with multianvil apparatus, following the azide route. The crystal structures of  $CaP_8N_{14}$  and  $SrP_8N_{14}$  are isotopic. The space group  $Cmcm$  was confirmed by powder X-ray diffraction. The structure of  $BaP_8N_{14}$  (space group  $Amm2$ ) was elucidated by a combination of transmission electron microscopy and diffraction of microfocused synchrotron radiation. Phase purity was confirmed by Rietveld refinement.

IR spectra are consistent with the structure models and the chemical compositions were confirmed by X-ray spectroscopy. Luminescence properties of  $Eu^{2+}$ -doped samples were investigated upon excitation with UV to blue light.  $CaP_8N_{14}$  ( $\lambda_{em} = 470$  nm;  $fwhm = 1380$   $cm^{-1}$ ) and  $SrP_8N_{14}$  ( $\lambda_{em} = 440$  nm;  $fwhm = 1350$   $cm^{-1}$ ) can be classified as the first ultra-narrow-band blue-emitting  $Eu^{2+}$ -doped nitridophosphates.  $BaP_8N_{14}$  shows a notably broader blue emission ( $\lambda_{em} = 417/457$  nm;  $fwhm = 2075/3550$   $cm^{-1}$ ).

## Introduction

The importance of advanced, highly efficient phosphor materials is continuously growing, as phosphor-converted light-emitting diodes (pc-LEDs) have revolutionized the global lighting market with increased durability, colour rendering and enormous energy savings. This technique uses blue-emitting primary LEDs, mostly based on InGaN, which are coated with phosphors to achieve emission of white light by colour mixing. Demands on potential coatings are manifold and reach from chemical and thermal stability, efficient absorption of blue light (primary LED) over optical transparency and a small

Stokes shift to high quantum efficiency and low thermal quenching.<sup>[1]</sup>

The most common coating for pc-LEDs is the oxide phosphor YAG:Ce ( $Y_{3-x}Gd_xAl_{5-x}Ga_xO_{12}:Ce^{3+}$ ).<sup>[2,3]</sup>  $Eu^{2+}$ -doped nitrides, however, show intense broad-band emission upon excitation with UV to blue light due to the parity-allowed  $4f^65d^1 \rightarrow 4f^7(^8S_{7/2})$  transition. (Oxo)nitridosilicates especially, have turned out to meet the above listed demands.  $AESi_2O_2N_2:Eu^{2+}$ ,  $AE_2Si_5N_8:Eu^{2+}$ , and the so far narrowest nitride-based  $Eu^{2+}$  red emitter  $Sr[Mg_3SiN_4]:Eu^{2+}$  have to be mentioned in this context.<sup>[4–8]</sup> Over the years, research on new phosphors expanded to a range of related compound classes, such as nitridoalumosilicates and nitridolithoaluminates, with  $Ca[AlSiN_3]:Eu^{2+}$  and  $Sr[LiAl_3N_4]:Eu^{2+}$  showing highly efficient red emission.<sup>[9,10]</sup> Recently, beryllium-containing nitrides have been shown to feature extremely narrow-band emissions in the blue to cyan spectral region.<sup>[11–13]</sup>

Nitridophosphates have repeatedly been discussed as phosphor materials as well, but only very few examples are known so far. The corresponding crystal structures are built up from anionic  $PN_4$  tetrahedra networks that host the cations.<sup>[14]</sup> Among ternary all-nitride representatives, only  $AEP_2N_4:Eu^{2+}$  ( $AE = Ca, Sr, Ba$ ) and  $Sr_3P_3N_7:Eu^{2+}$  are known.<sup>[15,16]</sup> However, these few members illustrate the versatility of nitridophosphates, as they cover a major part of the visible spectrum ( $\lambda_{emi} = 450–680$  nm) and also feature high quantum efficiencies even for non-optimized powder samples.<sup>[15–18]</sup> The great potential of nitridophosphates is underlined by zeolite-like compounds  $Ba_3P_5N_{10}X:Eu^{2+}$  ( $X = Cl, Br, I$ ), of which  $Ba_3P_5N_{10}Br:Eu^{2+}$  has to be highlighted, as it has been discussed as a natural-white-light single emitter.<sup>[17,18]</sup>

Fundamental research on nitridophosphates has established various synthetic approaches as recently reviewed in litera-

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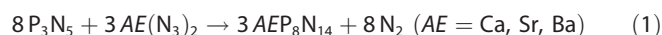
ture.<sup>[14]</sup> Alkaline earth nitridophosphates are commonly prepared in high-pressure high-temperature reactions starting from  $P_3N_5$  and the respective alkaline earth azide.<sup>[17–20]</sup> High-pressure conditions prevent the thermal decomposition of  $P_3N_5$  that otherwise starts at 850 °C and high-temperature enables the reversible cleavage and formation of P–N bonds.<sup>[21]</sup>

In our previous work, we have reported on synthesis of highly condensed  $SrP_8N_{14}$  following the azide route.<sup>[20]</sup> Considering its crystal structure, which features octahedrally coordinated Sr atom sites,  $SrP_8N_{14}$  and structurally related compounds appear as candidates for promising luminescence properties. In this contribution, we expand the  $AEP_8N_{14}$  system by the new compounds  $CaP_8N_{14}$  and  $BaP_8N_{14}$ , and discuss structural relations within this series of nitridophosphates. Furthermore, we present intriguing luminescence properties of all three  $Eu^{2+}$ -doped compounds that classify  $AEP_8N_{14}:Eu^{2+}$  as the first P/N-based ultra-narrow-band blue-light emitters.

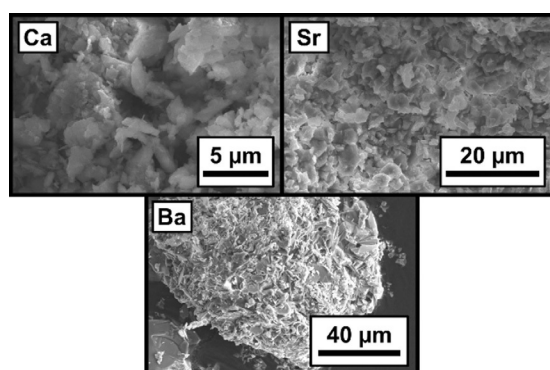
## Results and Discussion

### Synthesis

The nitridophosphates  $AEP_8N_{14}$  ( $AE=Ca, Sr, Ba$ ) were synthesized by high-pressure high-temperature reactions at 4–5 GPa and 1050–1150 °C, using a modified Walker-type multianvil apparatus.<sup>[22–26]</sup> The syntheses follow the azide route, starting from  $P_3N_5$  and the respective metal azide (Equation (1)). In order to investigate luminescence properties,  $Eu^{2+}$ -doped samples were obtained by addition of minor amounts of  $EuCl_2$  ( $\approx 3$  mole%) to the mixture of starting materials.



White ( $AEP_8N_{14}$ ) and yellowish ( $AEP_8N_{14}:Eu^{2+}$ ) products have been formed as microcrystalline powders and appeared stable against treatment with air and water (Figure 1).

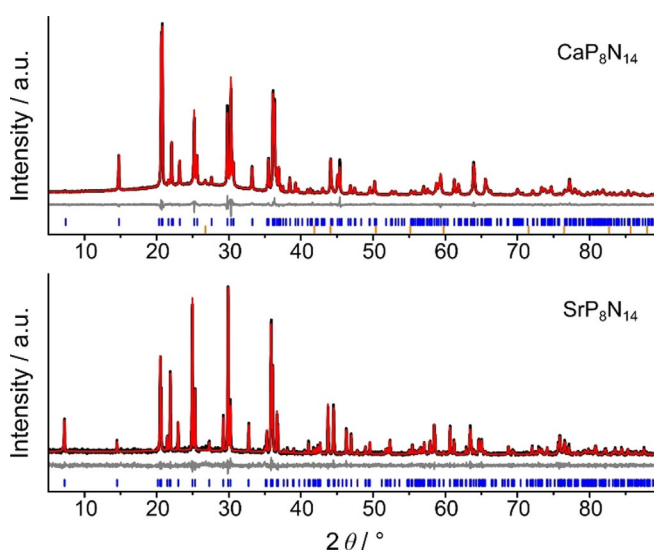


**Figure 1.** SEM images of  $AEP_8N_{14}:Eu^{2+}$  ( $AE=Ca, Sr, Ba$ ), illustrating the microcrystalline character of the samples.

### Structure elucidation

Owing to the lack of suitable single crystals, the structure of  $CaP_8N_{14}$  was refined from powder X-ray diffraction data em-

ploying the Rietveld method, where the published structure model of  $SrP_8N_{14}$  served as starting model (Figure 2).<sup>[20]</sup> The Rietveld method was further used to confirm phase purity of obtained  $SrP_8N_{14}$  (Figure 2). During refinement all atoms were refined with isotropic displacement parameters, using equal values for P and N atoms, respectively. Atomic coordinates and isotropic displacement parameters are listed in Tables S1 and S2 in Supporting Information. Detailed crystallographic information on the refinements of  $CaP_8N_{14}$  and  $SrP_8N_{14}$  is provided in Table S3. Further details on  $CaP_8N_{14}$  can be obtained from the Fachinformationszentrum Karlsruhe (FIZ) by quoting the deposition number CSD 1979592 via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).



**Figure 2.** Rietveld refinements for  $CaP_8N_{14}$  and  $SrP_8N_{14}$ : observed (black,  $Cu_{K\alpha_1}$ ) and calculated (red) powder X-ray diffraction patterns are displayed with corresponding difference profiles (gray). Vertical blue bars mark the Bragg reflections of the title compounds, orange bars mark the Bragg positions of h-BN (crucible material) that appeared as a minor side phase of  $CaP_8N_{14}$ .

At first glance, the PXRD pattern of  $BaP_8N_{14}$  bears similarities with those of  $AEP_8N_{14}$  ( $AE=Ca, Sr$ ) (Figure S1). However, corresponding Rietveld refinement did not yield reasonable results. Hence, a combination of transmission electron microscopy (TEM) and diffraction of microfocused synchrotron radiation was used for structure determination as described in previous works.<sup>[27,28]</sup> For this purpose, micron-sized crystals of  $BaP_8N_{14}$  were identified on a TEM grid by EDX analysis and selected area electron diffraction. Their precise positions were recorded (Figure S2) and single-crystal X-ray diffraction data were collected at the ESRF (beamline ID11) using a microfocused synchrotron beam (diameter  $\approx 1 \times 2 \mu m$ ).

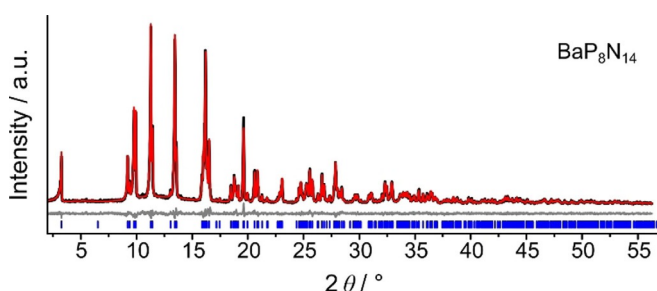
The crystal structure of  $BaP_8N_{14}$  was solved and refined in orthorhombic space group  $Amm2$  (no. 38) with unit cell dimensions  $a=12.4862(7)$ ,  $b=8.6648(3)$  and  $c=5.1373(2)$  Å. All atoms were refined anisotropically. Crystallographic data are summarized in the Supporting Information (Tables S4–S6) and can be obtained from the Fachinformationszentrum Karlsruhe

(FIZ) by quoting the deposition number CSD 1980141 via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

The refined structure model was used to verify the phase purity of  $\text{BaP}_8\text{N}_{14}$  by Rietveld refinement (Figure 3). More information on the Rietveld refinement for  $\text{BaP}_8\text{N}_{14}$  is provided in Table S7.

The chemical compositions of the title compounds were confirmed by energy-dispersive X-ray spectroscopy (EDX, Tables S8–S10). The spectra show trace amounts of oxygen, which may be attributed to partial surface hydrolysis during water treatment.

Fourier-transform infrared spectroscopy demonstrates the absence of N–H groups (Figures S4). The spectra feature only vibrations in the fingerprint region ( $400\text{--}1500\text{ cm}^{-1}$ ) and do not indicate N–H valence modes.



**Figure 3.** Rietveld refinement for  $\text{BaP}_8\text{N}_{14}\cdot\text{Eu}^{2+}$ ; observed (black,  $\text{MoK}_\alpha$ ) and refined (red) diffraction pattern. The difference profile is displayed in gray. Positions of Bragg reflections of  $\text{BaP}_8\text{N}_{14}$  are marked with vertical blue bars.

### Structure description

The compounds  $\text{AEP}_8\text{N}_{14}$  ( $\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$ ) can be classified as highly condensed nitridophosphates with a degree of condensation  $\kappa = 8/14 \approx 0.57$ , which is defined by the ratio of tetrahedra centres  $n(\text{P}) = 8$  to the number of N atoms  $n(\text{N}) = 14$ . All title compounds feature quadruple layers that are separated

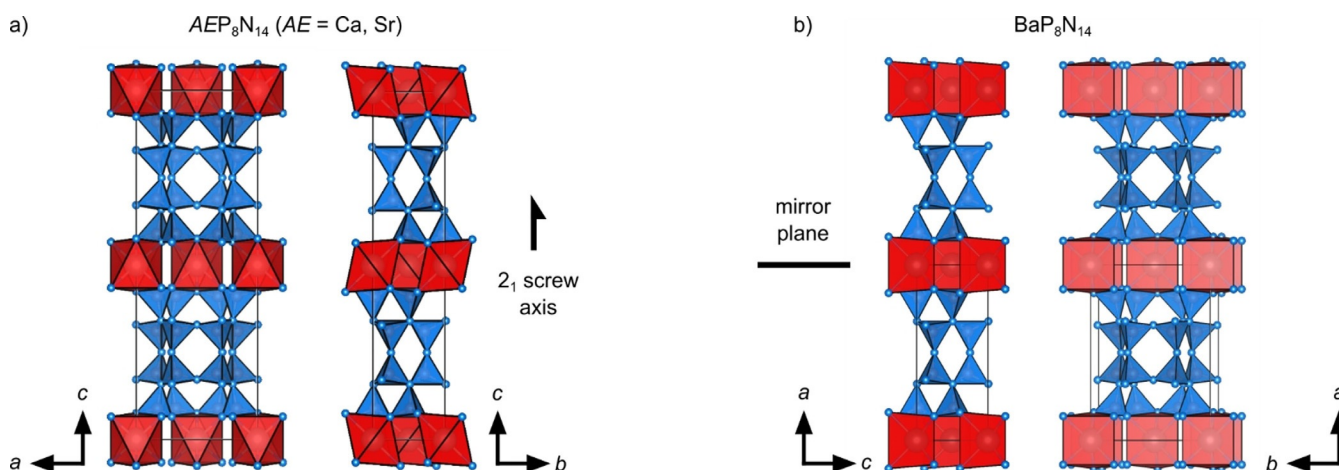
by metal atoms (Figure 4). A more detailed description of the layered structure is provided in literature and the Supporting Information (Figure S5).<sup>[20]</sup> The structure types of  $\text{AEP}_8\text{N}_{14}$  ( $\text{AE} = \text{Ca}, \text{Sr}$ ) and  $\text{BaP}_8\text{N}_{14}$  differ with respect to the stacking pattern of the quadruple layers. In  $\text{CaP}_8\text{N}_{14}$  and  $\text{SrP}_8\text{N}_{14}$ , these layers are related by rotation according to a  $2_1$  screw axis along [001] and by inversion symmetry. In the non-centrosymmetric structure of  $\text{BaP}_8\text{N}_{14}$ , however, they are related by a mirror plane  $\parallel$  (001) (Figure 4), resulting in a unit cell with half volume.

In  $\text{CaP}_8\text{N}_{14}$  and  $\text{SrP}_8\text{N}_{14}$ , the alkaline earth atom occupies one crystallographic site, that is octahedrally coordinated by N atoms with mean interatomic distances  $\text{AE-N}$  of 2.55 and 2.70 Å, respectively. In contrast, Ba occupies one crystallographic site, as well, but is located in a trigonal-prismatic coordination with a mean interatomic  $\text{Ba-N}$  distance of 2.83 Å. All observed  $\text{AE-N}$  distances are in good agreement with values of other known nitridophosphates as well as with the sums of the ionic radii.<sup>[15,17,18,20,29–31]</sup> This change of the coordination sphere is reminiscent of the  $\text{AEH}_4\text{P}_6\text{N}_{12}$  ( $\text{AE} = \text{Mg}, \text{Ca}, \text{Sr}$ ) compounds.<sup>[20,30]</sup> More detailed information on the coordination spheres in  $\text{AEP}_8\text{N}_{14}$  is provided in the Supporting Information (Figure S6 and Tables S11–S13).

For all title compounds, the P–N distances and N–P–N angles vary between 1.540(2)–1.737(4) Å and 103.1(2)–122.2(1)°, respectively, which is in good agreement with other nitridophosphates (Tables S11–S13).<sup>[15,17,18,20,29–31]</sup> The P–N distances dominate the coordination environments for N atoms with shorter distances for P–N<sup>[2]</sup> and slightly larger ones for P–N<sup>[3]</sup>.<sup>[32]</sup>

### Temperature dependent X-ray diffraction (HTXRD)

For the highly condensed nitridophosphates  $\text{AEP}_8\text{N}_{14}$  ( $\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$ ), significant thermal stability can be expected, considering the highly covalent character of the P–N network. Therefore, temperature dependent X-ray diffraction was carried out between room temperature and 950 °C (Figures S7–S9). The

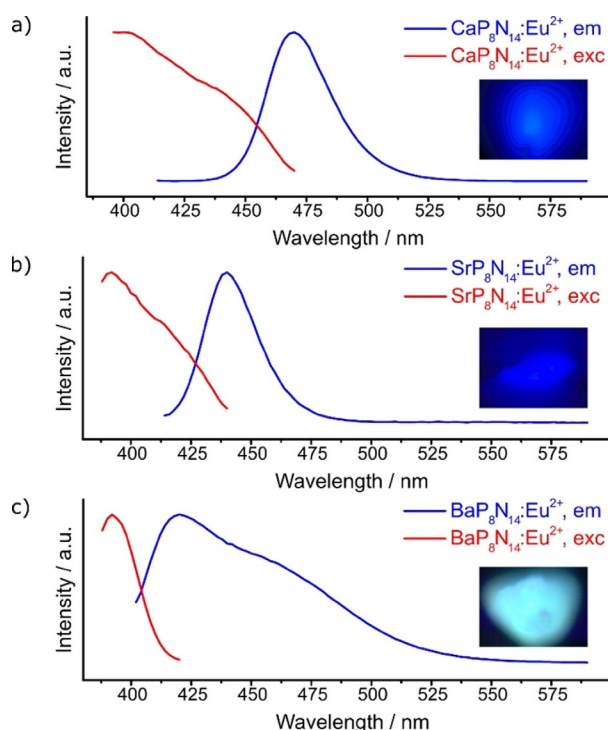


**Figure 4.** a) Projection of the crystal structure of  $\text{AEP}_8\text{N}_{14}$  ( $\text{AE} = \text{Ca}, \text{Sr}$ ) along [01 0] and [100]; b) projection of the crystal structure of  $\text{BaP}_8\text{N}_{14}$  along [0 1 0] and (approximately) [0 0 1]. The structural relation of neighbouring quadruple layers is indicated by the respective symmetry elements.  $\text{PN}_4$  tetrahedra are displayed in blue,  $\text{AEN}_6$  polyhedra in red. N atoms are depicted as blue spheres.

compounds are stable over this temperature range and diffraction patterns show nothing but a linear increase of lattice parameters (Figures S7–S12). A quantification of the respective thermal expansion was derived by Rietveld refinements for selected temperatures. It reveals an increase in volume of 1.0% to 1.8% with respect to ambient temperature (Tables S14 and S15).

## Luminescence

Considering the structural features as well as the chemical and thermal stability,  $AEP_8N_{14}$  ( $AE = Ca, Sr, Ba$ ) appeared as promising host materials for phosphors, and thus were doped with  $Eu^{2+}$  (nominal  $\approx 3$  mole% referred to  $AE^{2+}$ ) to investigate their luminescence properties. Upon excitation with near-UV to blue light, particles of all compounds show blue emission. Figures 5a and b show the excitation and emission spectra for  $CaP_8N_{14}:Eu^{2+}$  and  $SrP_8N_{14}:Eu^{2+}$ , respectively. According to a single crystallographic site for  $AE^{2+}$ , on which  $Eu^{2+}$  is expected to be localized, both compounds show only one emission band. Corresponding emission wavelengths ( $\lambda_{em}(CaP_8N_{14}:Eu^{2+}) = 470$  nm;  $\lambda_{em}(SrP_8N_{14}:Eu^{2+}) = 440$  nm) are comparable with other alkaline earth nitridophosphates, for example,  $BaP_2N_4:Eu^{2+}$  ( $\lambda_{em} = 454$  nm), despite the different coordination spheres of the activator ions (Table 1). Considering the fwhm of  $1380$   $cm^{-1}$  (31 nm) and  $1350$   $cm^{-1}$  (26 nm), respectively,  $CaP_8N_{14}:Eu^{2+}$  and  $SrP_8N_{14}:Eu^{2+}$  can be classified as the first P/N-based ultra-narrow-band blue emitters and can



**Figure 5.** Normalized excitation (red) and emission spectra (blue) of  $CaP_8N_{14}:Eu^{2+}$  (a),  $SrP_8N_{14}:Eu^{2+}$  (b), and  $BaP_8N_{14}:Eu^{2+}$  (c) measured at room temperature with respective micrographs of the measured crystals;  $\lambda_{exc}(CaP_8N_{14}:Eu^{2+}, SrP_8N_{14}:Eu^{2+}) = 400$  nm,  $\lambda_{exc}(BaP_8N_{14}:Eu^{2+}) = 390$  nm.

**Table 1.** Comparison of the luminescence properties at room temperature of  $AEP_8N_{14}:Eu^{2+}$  ( $AE = Ca, Sr, Ba$ ) with selected blue-emitting  $Eu^{2+}$ -doped (oxo)nitride materials.

Compound	CN	$\lambda_{em}$ [nm]	$\lambda_{exc}$ [nm]	Fwhm [nm]	Fwhm [ $cm^{-1}$ ]	Reference
$CaP_8N_{14}$	6	470	400	31	1380	This work
$SrP_8N_{14}$	6	450	400	26	1350	This work
$BaP_8N_{14}$	6	417	390	36	2075	This work
		457		$\approx 74$	3550	
$BaP_2N_4$	12	454	400	47	2244	[15]
$BaSr_2P_6N_{12}$	12	456	400	47	2240	[15]
$BaP_6N_{10}NH$	13	460	420	52	2423	[28]
$SrSi_8N_8$	10	450	370	44	–	[37]
$SrBe_{20}N_{14}$	12	428	380	22	1180	[11]
		540		$> 100$	–	
$BaBe_{20}N_{14}$	12	426	380	25	1310	[11]
		530		$> 110$	–	
$SrBe_6ON_4$	10	495	–	35	1400	[12]
$SrLi_2Be_4O_6$	8	456	400	25	1200	[13]
$BaLi_2Be_4O_6$	8	454	400	25	1200	[13]
$Sr_{0.25}Ba_{0.75}Si_2O_2N_2$	8	472	400	36	–	[4]
$BaSi_2O_2N_2$	8	492	450	37	–	[5]

compete with related (oxo)nitridoberyllate and —silicate phosphors.<sup>[4,11–13]</sup>

In contrast to  $CaP_8N_{14}:Eu^{2+}$  and  $SrP_8N_{14}:Eu^{2+}$ ,  $BaP_8N_{14}:Eu^{2+}$  shows a rather broad emission band at 417 nm (fwhm = 36 nm/2075  $cm^{-1}$ ) next to a significantly wider band at  $\approx 457$  nm (fwhm = 74 nm/3350  $cm^{-1}$ , Figure 5c). In order to elucidate the maxima and fwhm of this emission, the spectrum was deconvoluted with two pseudo-Voigt functions (Figure S13;  $\lambda_{em1} = 417$  nm,  $fwhm_1 = 36$  nm/2075  $cm^{-1}$ ,  $\lambda_{em2} = 457$  nm,  $fwhm_2 = 74$  nm/3350  $cm^{-1}$ ). The position of the first band fits well to the series of  $AEP_8N_{14}:Eu^{2+}$  ( $AE = Ca, Sr$ ) and is assigned to the one Ba site in  $BaP_8N_{14}$ . The second emission band can be explained by the comparison of the excitation spectra monitored at different wavelengths ( $\lambda_{mon} = 425$ –516 nm; Figure S14). Due to the very similar spectra for different  $\lambda_{mon}$ , the second emission band can unambiguously be assigned to the title compound as well, indicating large Stokes shifted impurity trapped exciton emission. Similar effects have already been observed for Ba compounds in literature.<sup>[33]</sup> The assumption that this artefact might be caused by a side phase can be excluded, as the emission band was observed in several phase-pure samples (Figure S15). The different relative intensities of the two emission bands in the different samples are most likely attributable to different excitation wavelengths (Figure S15). Characteristic parameters of the luminescent properties of  $AEP_8N_{14}:Eu^{2+}$  ( $AE = Ca, Sr, Ba$ ) are listed in Table 1, providing a brief comparison with other relevant blue phosphors.

## Conclusions

In this contribution, we report on syntheses of the highly condensed nitridophosphates  $AEP_8N_{14}$  ( $AE = Ca, Sr, Ba$ ) and illustrate their structural relation. Although all three compounds feature quadruple layers separated by metal atoms, only

SrP<sub>8</sub>N<sub>14</sub> and CaP<sub>8</sub>N<sub>14</sub> proved isotypic. The structure of BaP<sub>8</sub>N<sub>14</sub> as refined from diffraction data using microfocused synchrotron radiation differs in the orientation of these layers. Here, the layer stacking leads to a trigonal-prismatic environment of Ba<sup>2+</sup>, while Ca<sup>2+</sup> and Sr<sup>2+</sup> are coordinated in octahedral fashion. Corresponding luminescence investigations on Eu<sup>2+</sup>-doped samples show blue emission upon excitation with UV to blue light. The extremely narrow emission bands of CaP<sub>8</sub>N<sub>14</sub>:Eu<sup>2+</sup> and SrP<sub>8</sub>N<sub>14</sub>:Eu<sup>2+</sup> render these compounds competitive phosphors in comparison with other established classes of compounds. Especially, the Ca compound with its small Stokes shift shows very attractive luminescence properties for an application in solid-state lighting, because the lowest lying absorption band matches very well in spectral position with blue emitting InGaN LEDs. Hence, the spectral emission intensity distribution can lower the spectral gap between blue pump LED and green phosphor emission which is typically being observed in state-of-the-art white pc-LEDs. Filling this „cyan gap“ of a white spectrum will significantly enhance colour rendition of a light source.<sup>[34,35]</sup> Moreover, pronounced thermal stability and absence of toxic elements further highlight the great potential of the AEP<sub>8</sub>N<sub>14</sub>:Eu<sup>2+</sup> compounds. Future studies may thus focus on an alternative synthetic access in order to provide the preconditions for industrial application. Ammonothermal synthesis appears promising, as such syntheses of partially crystalline SrP<sub>8</sub>N<sub>14</sub> have already been reported.<sup>[36]</sup> Moreover, such methods could provide sufficient sample quantities for a more precise characterization of the luminescence performance, meaning for example, temperature-dependent emission spectra.

## Experimental Section

**Synthesis of P<sub>3</sub>N<sub>5</sub>:** P<sub>3</sub>N<sub>5</sub> was synthesized by ammonolysis starting from P<sub>4</sub>S<sub>10</sub> (ca. 7.0 g, Sigma Aldrich 99.99%) in a tube furnace lined with a silica tube. The apparatus, including the silica reaction boat, was heated for 4 h at 1000 °C under vacuum ( $\leq 10^{-3}$  mbar) for drying. Subsequently, the starting material was loaded into the reaction boat under Ar flow. Only a limited amount of P<sub>4</sub>S<sub>10</sub> can be used, as otherwise the reaction tube may be clogged by by-products. After saturating the atmosphere in the silica tube for 4 h with a constant flow of dried NH<sub>3</sub> ( $\approx 3.6$  L h<sup>-1</sup>, Air Liquide 5.0), P<sub>4</sub>S<sub>10</sub> was heated to 850 °C (rate: 5 °C min<sup>-1</sup>) and held at this temperature for 4 h. Finally, the furnace was allowed to cool down to room temperature (rate: 5 °C min<sup>-1</sup>) and the apparatus was flushed with Ar for 1 h in order to remove remaining NH<sub>3</sub>. The recovered product showed orange coloured grains, which were purified by washing with water, ethanol, and acetone. Further information on the synthesis are given in literature.<sup>[38–40]</sup> P<sub>3</sub>N<sub>5</sub> was identified by powder X-ray diffraction and FTIR spectroscopy.

**Synthesis of AE(N<sub>3</sub>)<sub>2</sub> (AE = Ca, Sr, Ba):** Alkaline earth azides AE(N<sub>3</sub>)<sub>2</sub> (AE = Ca, Sr, Ba) were synthesized by reactions of the respective alkaline earth carbonates (CaCO<sub>3</sub>: Alfa Aesar, 99.5%; SrCO<sub>3</sub>: Sigma Aldrich, 99.995%; BaCO<sub>3</sub>: Grüssing, 99.8%) with HN<sub>3</sub> prepared by means with a cation exchanger (Amberlyst 15) according to the procedure described by Suhrmann and modified by Karau.<sup>[38,41]</sup> A diluted solution of HN<sub>3</sub> is formed in situ by passing an aqueous solution of NaN<sub>3</sub> (Acros Organics, 99%, extra pure) through the cation exchanger. HN<sub>3</sub> then drops into a stirred aqueous suspen-

sion of the carbonate until the eluate shows a neutral pH value and the solution turns clear. Residues of the carbonate were filtered off and the solvent was removed with a rotary evaporator (50 mbar, 40 °C). The products were obtained as colourless fine powders, which were recrystallized from acetone and dried under vacuum. AE(N<sub>3</sub>)<sub>2</sub> (AE = Ca, Sr, Ba) were investigated for purity by powder X-ray diffraction and FTIR spectroscopy. **Caution:** Since HN<sub>3</sub> is potentially explosive and highly poisonous in its gaseous form, special care is necessary.

**Synthesis of AEP<sub>8</sub>N<sub>14</sub> (AE = Ca, Sr, Ba):** The nitridophosphates AEP<sub>8</sub>N<sub>14</sub> (AE = Ca, Sr, Ba) were obtained by high-pressure high-temperature synthesis using a 1000 t press with a modified Walker-type multianvil apparatus.<sup>[22–26]</sup> All products were synthesized from stoichiometric amounts of P<sub>3</sub>N<sub>5</sub> and the respective alkaline earth azide (see Supporting Information, Table S16). Owing to the high air-sensitivity of the azides, the starting materials were handled in an Ar-filled glovebox (Unilab, MBraun, Garching, O<sub>2</sub> < 1 ppm, H<sub>2</sub>O < 0.1 ppm) and ground thoroughly in an agate mortar. The mixture was transferred into a cylindrical crucible made from hexagonal boron nitride (HeBoSint® S100, Henze, Kempten, Germany) and sealed with a boron nitride cap. The crucible was then placed in a specially prepared octahedron (MgO, doped with Cr<sub>2</sub>O<sub>3</sub> (5%), edge length 18 mm, Ceramic Substrates & Components, Isle of Wight, UK), which was drilled through and loaded with different components. First, a ZrO<sub>2</sub> sleeve (Cesima Ceramics, Wust-Fischbeck, Germany) was fixed in the borehole and closed on one side by a Mo plate. Then, a long graphite tube (Schunk Kohlenstofftechnik GmbH, Gießen, Germany), a MgO spacer (Cesima Ceramics, Wust-Fischbeck, Germany) and a short graphite tube were put into the octahedron. While ZrO<sub>2</sub> served as thermal insulator, the two graphite tubes were used as electrical resistance furnace, whereby the combination of two single tubes is necessary to decrease the temperature gradient. After inserting the crucible with the sample, the assembly was completed by adding a second MgO spacer and a further Mo plate to ensure a symmetric setup. In order to generate approximately hydrostatic conditions, the uniaxial force of the hydraulic press was converted by a Walker-type module with inserted steel wedges, forming a cubic cavity. This cavity was filled by eight Co-doped (7%) WC cubes (Hawedia, Marklkofen, Germany). To enclose the sample octahedron, the edges of the WC cubes were truncated (11 mm edge length). Furthermore, four of the cubes were equipped with a PTFE film (Vitaflon Technische Produkte GmbH, Bad Kreuznach, Germany) for electrical insulation. The remaining cubes were prepared with pyrophyllite gaskets (Cermaic Substrates & Components, Isle of Wight, UK) to prevent the outflow of the MgO octahedron. Bristol board (369 g m<sup>-2</sup>) was used to fix the gaskets. Further information on the experimental high-pressure setup is given in the literature.<sup>[42]</sup> Different pressure and temperature settings were used (CaP<sub>8</sub>N<sub>14</sub>: 5 GPa,  $\approx 1075$  °C; SrP<sub>8</sub>N<sub>14</sub>: 5 GPa,  $\approx 1075$  °C; BaP<sub>8</sub>N<sub>14</sub>: 4 GPa,  $\approx 1150$  °C). Detailed programs are given in Table S17.

**Scanning electron microscopy (SEM) and energy-dispersive X-ray diffraction (EDX):** The morphology of the samples was investigated with a Dualbeam Helios Nanolab G3 UC (FEI, Hillsboro). An X-Max 80 SDD EDX detector (Oxford Instruments, Abingdon) was used for chemical analyses. An adhesive carbon film was used to fix the samples on a holder. To ensure electrical conductivity, the samples were coated with carbon with an electron beam evaporator (BAL-TEC MED 020, Bal Tec AG). Data were analyzed with the Aztec software.<sup>[43]</sup>

**Transmission electron microscopy (TEM):** The sample was ground in an agate mortar, suspended in ethanol and drop-cast on a copper grid with holey carbon film (S160NH2C, Plano GmbH, Wet-

zlar, Germany). The grid was mounted on a double-tilt holder and isolated crystallites of  $\text{BaP}_8\text{N}_{14}$  were identified by EDX and electron diffraction using a FEI Tecnai G20 transmission electron microscope (TEM) with a thermal emitter ( $\text{LaB}_6$ ) operated at 200 keV. Selected area electron diffraction patterns and bright-field images were recorded using a TVIPS camera (TemCam F216, Tietz) with a resolution of  $2048 \times 2048$  pixels.

**Single-crystal X-ray diffraction:** The TEM grid was mounted on a Symétrie Hexapods Nanopos device. A  $\text{BaP}_8\text{N}_{14}$  crystal of about  $2 \times 3 \times 0.5 \mu\text{m}$  in size was recovered at beamline ID11 ( $\lambda = 0.309 \text{ \AA}$ , ESRF, Grenoble) by a telescope with large magnification, using the copper crossbars of the grid as landmarks. The crystallite was centred using Ba X-ray fluorescence scans. The single-crystal data set was then collected using a microfocused synchrotron beam of  $1 \times 2 \mu\text{m}$ . CrysAlisPro and SADABS were used for the integration and the semiempirical absorption correction of the data.<sup>[44,45]</sup> The incomplete absorption of X-ray radiation in the CCD phosphor was corrected.<sup>[46]</sup> The crystal structure was solved by direct methods and refined by least-squares methods with SHELX-2014.<sup>[47]</sup>

CCDC 1979592 (Ca) and 1980141 (Ba) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre through the CCDC/FIZ Karlsruhe joint deposition service.

**FTIR spectroscopy:** FTIR spectra of the title compounds were collected on a Spectrum BX II spectrometer (PerkinElmer, Waltham, MA, USA) between 600 and  $4000 \text{ cm}^{-1}$  with DuraSampler attenuated total reflectance unit (ATR).

**Powder X-ray diffraction:** Powder X-ray diffraction data were collected with a Stoe Stadi P diffractometer with  $\text{Cu}_{K\alpha 1}$  ( $\lambda = 1.5406 \text{ \AA}$ ) or  $\text{Mo}_{K\alpha 1}$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. The diffractometers were equipped with Ge(111) monochromators and Mythen 1 K Si strip detectors (Dectris, Baden, Switzerland). The ground samples were transferred into glass capillaries with 0.3 mm diameter (Hilgenberg GmbH, Malsfeld, Germany). The TOPAS Academic 6.1 package was used for Rietveld refinements using the fundamental parameters approach and a shifted Chebyshev function for handling the background.<sup>[48]</sup> Temperature dependent powder X-ray diffraction data were collected on a Stoe Stadi P diffractometer ( $\text{Mo}_{K\alpha 1}$  radiation; Ge(111) monochromator) with a resistance graphite furnace (Stoe) and IP-PSD detector. Samples were loaded into fused silica capillaries (0.5 mm diameter) and heated from room temperature to  $950 \text{ }^\circ\text{C}$  with steps of  $25 \text{ }^\circ\text{C}$  and a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ . At each step data were collected with constant temperature.

**Luminescence:** Luminescence spectra of  $\text{Eu}^{2+}$ -doped samples ( $\approx 3$  mole%) were examined on a HORIBA Fluoromax4 spectrofluorimeter system with Olympus BX51 microscope. Emission spectra were collected at room temperature with  $\lambda_{\text{exc}} = 400 \text{ nm}$  for  $\text{AE} = \text{Ca}$ ,  $\text{Sr}$ , and  $\lambda_{\text{exc}} = 390 \text{ nm}$  for  $\text{Ba}$ , respectively, in a range from 400 to 800 nm (step width: 2 nm). Excitation spectra were recorded with monitoring wavelength  $\lambda_{\text{mon}}$  from 425 to 516 nm.

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## Conflict of interest

The authors declare no conflict of interest.

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