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$Ba_3P_5N_{10}Br{:}Eu^{2+}$: A Natural-White-Light Single Emitter with a Zeolite Structure Type**

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Abstract: *Illumination sources based on phosphor-converted light emitting diode (pcLED) technology are nowadays of great relevance. In particular, illumination-grade pcLEDs are attracting increasing attention. Regarding this, the application of a single warm-white-emitting phosphor could be of great advantage. Herein, we report the synthesis of a novel nitridophosphate zeolite* $Ba_3P_5N_{10}Br{:}Eu^{2+}$*. Upon excitation by near-UV light, natural-white-light luminescence was detected. The synthesis of* $Ba_3P_5N_{10}Br{:}Eu^{2+}$ *was carried out using the multianvil technique. The crystal structure of* $Ba_3P_5N_{10}Br{:}Eu^{2+}$ *was solved and refined by single-crystal X-ray diffraction analysis and confirmed by Rietveld refinement and FTIR spectroscopy. Furthermore, spectroscopic luminescence measurements were performed. Through the synthesis of* $Ba_3P_5N_{10}Br{:}Eu^{2+}$*, we have shown the great potential of nitridophosphate zeolites to serve as high-performance luminescence materials.*

Zeolites find application in numerous technological areas worldwide and have become an irreplaceable materials class in modern industry. Classical zeolites, such as aluminosilicates and aluminophosphates, are widely used, for example in the fields of petroleum refining, in the petrochemical and fine chemical industry as adsorbents, and as ion exchangers or catalysts. Furthermore, this compound class also has the potential for further applications in future technologies, for example in sensors and electronic or optical systems.[1–6] Prominent examples of the commercially most important functional zeolites are $Na_x(H_2O)_{16}Al_xSi_{96\text{-}x}O_{192}$ ($x < 27$; ZSM-5) and $Na_{12}(H_2O)_{27}[Al_{12}Si_{12}O_{48}]_8$ (LTA), which exhibit excellent chemical and thermal stability.[7,8]

Conventional oxidic zeolite structures are typically composed of a three-dimensional network of vertex-sharing $[SiO_4]$ and $[AlO_4]$ tetrahedra, in which a negative charge is associated with each $[AlO_4]$ tetrahedron.[9,10] Given that the element combination P/N is isoelectronic to Si/O, it is reasonable to expect that the resulting compound class of nitridophosphates exhibits a structural variety similar to or even more diverse than that of silicates. The formal substitution of O atoms by N atoms in a tetrahedral network implies significant new structural possibilities. The structural diversity of oxosilicates is limited to terminal or singly bridging O atoms, whereas N atoms in nitridophosphates may occur as $N^{[1]}$, $N^{[2]}$, $N^{[3]}$, or even $N^{[4]}$ atoms.[11] (The superscripted numbers in square brackets following element symbols define their coordination numbers.) Furthermore, nitridic zeolites promise useful chemical and physical properties (for example, adjustable acidity/basicity). A prominent example for these extended structural possibilities of nitridophosphates as well as their potential in the field of open-framework structures is the nitridic clathrate $P_4N_4(NH)_4(NH_3)$ that was discussed as a possible gas-storage material.[12,13] Its network structure has been predicted for silica but to date has only been found in this particular nitride compound. Furthermore, two nitridic zeolites in the compound class of nitridophosphates are known to date, namely $Li_xH_{12-x-y+z}[P_{12}O_yN_{24-y}]X_z$ ($X = Cl$, Br) and $Ba_{19}P_{36}O_{6+x}N_{66-x}Cl_{8+x}$ ($x \approx 4.54$). Both represent unusual network structure types, namely NPO (nitridophosphate one) and NPT (nitridophosphate two), respectively.[14–17]

As a result of their high thermal and chemical stability as well as highly cross-linked network structures, nitridic zeolites are basically well suited as host lattices for Eu^{2+} doping. Consequently, new interesting luminescent materials may be expected with possible application in phosphor-converted light-emitting diodes (pcLEDs). The constantly growing relevance of pcLEDs makes further investigation of luminescent materials an important research target. In particular, white light sources based on LED technology are gaining increasing attention. The Nobel Prize in Physics 2014 that was awarded to Akasaki, Amano, and Nakamura “*for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources*” confirms this assessment.[18] Several strategies are available to obtain high quality pcLEDs for illumination. The strategy adopted in industry is based on the multiphosphors-conversion model.[19,20] In this case, for example, green (e.g. $Lu_3Al_5O_{12}{:}Ce^{3+}$),[21] red (e.g. $(Ba,Sr)_2Si_5N_8{:}Eu^{2+}$),[22,23] and yellow (e.g. Ca-α-SiAlON:Eu^{2+})[24,25] emitting phosphors are mixed and coated on an InGaN semiconductor LED chip to achieve white light. The main problem of this strategy, however, is the differing thermal stability of the individual phosphors, which often results in poor emission-color stability. Moreover, the particle sizes of individual phosphor materials have to be adapted to one another to avoid agglomeration. Finally, the individual phosphors have to be mixed very homogeneously in exact ratios. To alleviate these

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difficulties, application of a single white-emitting phosphor could be of great advantage. Several compounds, such as $Ba_{1.3}Ca_{0.7}SiO_4$:Eu^{2+},Mn^{2+},[26] $Ba_3MgSi_2O_8$:Eu^{2+},Mn^{2+},[27] and $CaAl_2Si_2O_8$:Eu^{2+},Mn^{2+}[28] have been already investigated as promising single-phase phosphors for near-UV white LEDs. However, the co-doping with Eu^{2+} and Mn^{2+} ions may lead to poor emission-color stability because of the different emitting centers which exhibit different thermal-quenching behaviors.

In this Communication, we report the synthesis and structural investigation of the novel nitridophosphate $Ba_3P_5N_{10}Br$ with a zeolite-type structure. Doped with Eu^{2+}, $Ba_3P_5N_{10}Br$ exhibits natural-white-light luminescence upon excitation by near-UV light, making this compound a promising candidate for use as a single white emitter in pcLEDs.

$Ba_3P_5N_{10}Br$:Eu^{2+} was synthesized by the reaction of stoichiometric amounts of $Ba(N_3)_2$, $BaBr_2$, and P_3N_5 according to Equation (1). $EuCl_2$ (2 mol%) was used as the doping agent. The synthesis was carried out using a Walker-type multianvil assembly and a 1000 t hydraulic press at pressures between 1 and 5 GPa and 1000 °C for 30 minutes.[29] Through the thermolysis of $Ba(N_3)_2$ a high N_2 partial pressure is available. It prevents P_3N_5 from dissociation into its composite elements under high pressure at reaction temperatures above 1000 °C.[30] At ambient pressure, P_3N_5 already decomposes at temperatures above 850 °C. The product was obtained as an air-stable colorless (light yellow when doped with Eu^{2+}) crystalline solid (see Figure 1). To grow single crystals of the compound which are large enough to be suitable for single-crystal X-ray diffraction, the heating time was increased up to 200 minutes.

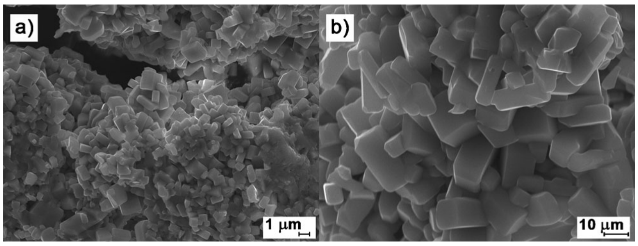

Figure 1. SEM images of crystals of $Ba_3P_5N_{10}Br$:Eu^{2+} measured on a) 1 µm or b) 10 µm scale.

$$15\,Ba(N_3)_2 + 3\,BaBr_2 + 10\,P_3N_5 \rightarrow 6\,Ba_3P_5N_{10}Br + 40\,N_2 \qquad (1)$$

At ambient pressure, the synthesis of $Ba_3P_5N_{10}Br$ was also accomplished by heating a mixture of $BaBr_2$, amorphous HPN_2, and NH_4Br as mineralizer in evacuated and sealed silica ampoules to 800 °C for 84 h. A similar approach has been already applied for the synthesis of various nitridophosphates exhibiting a sodalite-type structure.[16,31] However, by this procedure $Ba_3P_5N_{10}Br$ was only accessible as a minor side phase. To obtain a single-phase product, the reaction conditions as well as the starting materials have to be optimized. In addition to the starting materials named above, BaH_2 and $P(NH_2)_4Br$[32] may be used.

To clarify the chemical composition of the product, energy-dispersive X-ray (EDX) spectroscopy has been carried out. No elements other than Ba, P, N, and Br were detected. The determined atomic ratio Ba/P/N/Br is in good agreement with the predicted composition $Ba_3P_5N_{10}Br$ (see Table S1 in the Supporting Information).

The crystal structure of $Ba_3P_5N_{10}Br$:Eu^{2+} was solved and refined from single-crystal X-ray diffraction data in the orthorhombic space group *Pnma* (no. 62) using direct methods.[33] As a result of the elongated displacement ellipsoid of the N11 atom, it was possible to refine a split position for this atom with occupancy of approximately 0.5 each (Figure S1). All atom positions were refined anisotropically. As a result of the small crystal size as well as significant differences in the X-ray scattering power of N atoms compared to Ba and Br atoms, a common anisotropic displacement parameter for the N atom positions was refined. The accuracy of the structure elucidation as well as phase purity of the product was confirmed by Rietveld refinement (Figure 2). The crystallographic details are summarized in the Supporting Information.

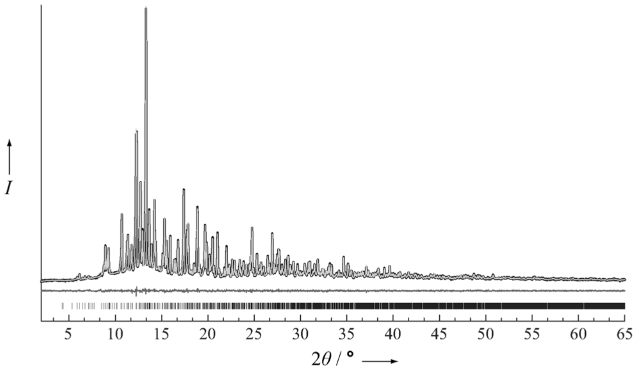

Figure 2. Experimentally observed (black line) and calculated (light gray line) X-ray powder diffraction pattern, positions of Bragg reflections (vertical bars) and difference profile (dark gray line) for the Rietveld refinement of $Ba_3P_5N_{10}Br$:Eu^{2+}.

The crystal structure of $Ba_3P_5N_{10}Br$ consists of a network of all-side vertex-sharing PN_4 tetrahedra, leading to three-dimensional *achter*-ring channels, according to the nomenclature introduced by Liebau.[10] These channels contain alternately Ba and Br atoms (Figure 3). The PN_4 tetrahedra form condensed *dreier*, *vierer*, and *achter* rings. This condensation results in turn in two slightly distorted CBUs (composite building unit) both forming $3^4 4^2 8^6$ cages (Figure 4). Both cages exhibit the same basic atom arrangement but differ slightly in their degree of deformation.

The centers of the CBUs are occupied by Br atoms, which are coordinated by six Ba atoms in a distorted octahedral arrangement (Figure 4). These BaN_6 octahedra are connected to each other via shared edges forming a three-dimensional network.

The framework topology of $Ba_3P_5N_{10}Br$ was determined by the TOPOS software.[34] It is represented by the point symbol $(3.4.5.8^3)_4(3^2.8^4)$ and is analogous to the topology of

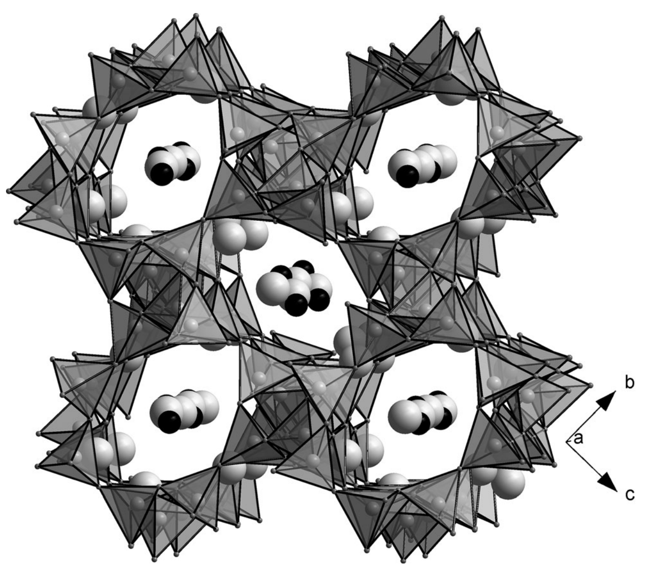

Figure 3. Crystal structure of $Ba_3P_5N_{10}Br$, viewed along [100]. Atom colors: Ba = light gray, Br = black, PN_4 tetrahedra = dark gray.

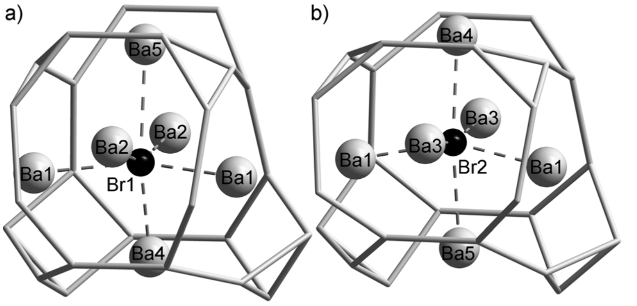

Figure 4. Topological representation of the two different $3^44^28^6$ cages with cage content in $Ba_3P_5N_{10}Br$ with each connecting line representing a P–N–P bond. Atom colors (spheres): Ba = light gray, Br = black.

the JOZ zeolite framework type.[17,35] Despite this structural analogy $Ba_3P_5N_{10}Br$ is not porous and thus not prone to sorption of water and hydrolysis.

The P–N bond lengths range between 1.607 and 1.637 Å and lie in the range of those usually observed in similar nitridophosphates.[36,37] The N-P-N angles vary between 99.4 and 119.3° and thus differ slightly from the regular tetrahedral angle. However, the range is typical of other nitridophosphate zeolites.[15,16]

The crystal structure of $Ba_3P_5N_{10}Br$ contains five different crystallographic Ba positions, whose coordination spheres are shown in Figure 5. Ba1 is coordinated ninefold by seven N atoms (2.790–3.314 Å) and two Br atoms (3.341 and 3.391 Å). The Ba2 and Ba3 positions are coordinated by six N atoms (2.753–3.009 Å) and two Br atoms (3.174–3.241 Å), respectively, forming slightly distorted hexagonal bipyramids. In contrast, the coordination spheres of Ba4 and Ba5 centers represent irregular polyhedra consisting of eight N atoms (2.713–3.347 Å) and two Br atoms (3.360–3.668 Å). The N11a and N11b atoms represent one split position of the N11 position. All bond lengths Ba–N and Ba–Br correspond to those in other known compounds as well as to the sum of the ionic radii.[36–40]

The absence of N–H groups in $Ba_3P_5N_{10}Br{:}Eu^{2+}$ was confirmed by FTIR spectroscopy (Figure S2). The FTIR spectrum shows several groups of bands below 1500 cm^{-1}. These can be attributed to symmetric and asymmetric P–N–P stretching modes, respectively. However, there are no absorption bands around 3000 cm^{-1}, which would be typical for N–H valence vibrations.

By doping of $Ba_3P_5N_{10}Br$ with Eu^{2+} ions, natural-white-light luminescence was detected upon excitation by near-UV light ($\lambda = 400$ nm). Figure 6 displays the excitation and emission spectra of $Ba_3P_5N_{10}Br{:}Eu^{2+}$ crystallites. The excitation spectrum reveals a maximum at $\lambda = 396$ nm. Thus, this compound can be effectively excited by near-UV light. Excitation at $\lambda = 400$ nm results in an emission spectrum with two bands: one in the blue spectral region centered at $\lambda = 472$ nm, and the other in the yellow spectral region centered at $\lambda = 582$ nm. The values of the full width at half maximum (FWHM) are approximately 1502 cm^{-1} (for the band at $\lambda = 472$ nm) and 2374 cm^{-1} (for the band at $\lambda = 582$ nm). The presence of two emission bands can be explained by occupation of Eu^{2+} ions on different Ba lattice sites. The example of $Ba_3MgSi_2O_8{:}Eu^{2+},Mn^{2+}$ demonstrates that the differences in the coordination polyhedra of the different Ba lattice sites has a strong influence on the number of emission bands.[27] The combination of both emission bands generates the resulting natural-white-light luminescence of the title compound with a correlated color temperature (CCT) of 3384 K, lumen equivalent of 372 lm/W, and CIE

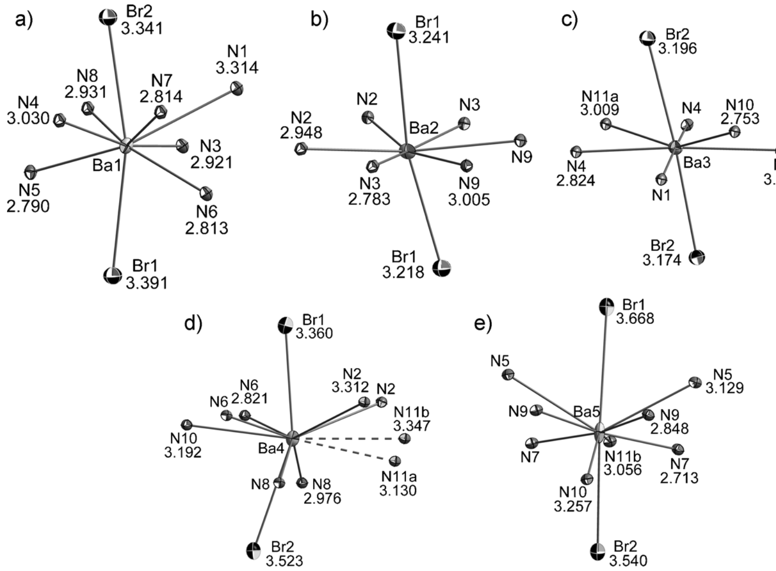

Figure 5. Coordination polyhedra and corresponding bond lengths [Å] of the a) Ba1, b) Ba2, c) Ba3, d) Ba4, and e) Ba5 positions in the crystal structure of $Ba_3P_5N_{10}Br$. Thermal ellipsoids are set at 70% probability.

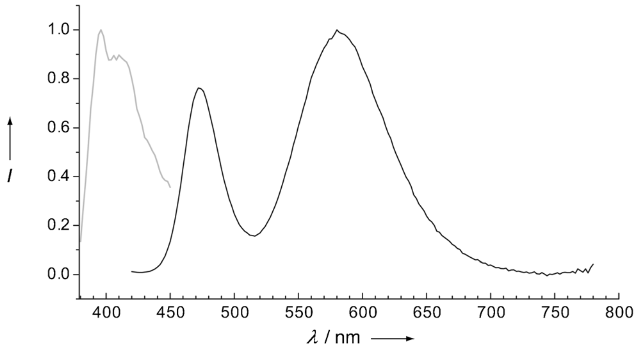

Figure 6. Excitation (gray) and emission (black) spectra of $Ba_3P_5N_{10}Br{:}Eu^{2+}$. Excitation spectrum: $\lambda_{exc,max} = 396$ nm. Emission spectrum: $\lambda_{exc} = 400$ nm. CIE color coordinates: $x = 0.415$, $y = 0.403$.

color coordinates $x = 0.415$, $y = 0.403$. The quantum efficiency of a powder sample is close to 63% for $\lambda = 390$ nm excitation. In this context it should be noted that the quantum efficiency was determined for a non-optimized sample. By optimizing the Eu^{2+} doping level in the sample the quantum efficiency could be certainly increased. Detailed information on the luminescent measurements is summarized in the Supporting Information.

To investigate the thermal stability of $Ba_3P_5N_{10}Br{:}Eu^{2+}$ temperature dependent powder X-ray diffraction up to 1000 °C was performed. The results (Figure S3) show that the sample is stable in air up to at least 1000 °C. Furthermore, resistance against hydrolysis of $Ba_3P_5N_{10}Br{:}Eu^{2+}$ was checked by storing the sample under water for several days. However, neither a quenching of the luminescence nor the decomposition of the sample was observed.

In this Communication we presented a novel nitridophosphate $Ba_3P_5N_{10}Br$ with a zeolite-type structure. We were able to characterize this compound by single-crystal X-ray diffraction, powder X-ray diffraction, FTIR, and EDX spectroscopy. The topology of $Ba_3P_5N_{10}Br$ corresponds to that of the JOZ zeolite structure type. Doped with Eu^{2+}, the title compound exhibits natural-white-light luminescence upon excitation by near-UV light. This feature makes $Ba_3P_5N_{10}Br{:}Eu^{2+}$ a promising candidate for use as a single white emitter in pcLEDs. Moreover, using the example of $Ba_3P_5N_{10}Br{:}Eu^{2+}$, we have demonstrated that nitridic zeolites are well suited as host lattices for high-performance luminescence materials. Consequently, the synthesis of isotypic compounds $M_3P_5N_{10}X{:}Eu^{2+}$ by the exchange of halide ion X or alkaline-earth ion M may lead to further interesting luminescent properties.

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[33] Crystal data for $Ba_3P_5N_{10}Br$: crystal size: $0.010 \times 0.020 \times 0.020\ mm^3$, space group *Pnma* (no. 62), $a = 12.5660(13)$, $b = 13.2240(13)$, $c = 13.8030(14)$ Å, $V = 2293.7(4)$ Å^3, $Z = 8$, $\rho_{diff} = 4.557\ g\,cm^{-3}$, Bruker D8 Venture, Mo-$K_\alpha$ radiation (71.073 pm), multi-scan absorption correction, 31838 reflections, 2354 independent reflections, $R_{int} = 0.0735$, least-squares refinement on F^2, R values (all data/$F_o^2 \geq 2\sigma(F_o^2)$): $R_1 = 0.0457/0.0339$,

$wR_2 = 0.0658/0.0638$, GooF = 1.216 for 1960 observed reflections ($F_o^2 \geq 2\sigma(F_o^2)$) and 132 parameters. 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-428381.

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