Inverse-Tunable Red Luminescence and Electronic Properties of Nitridoberylloaluminates Sr$_{2-x}$Ba$_x$[BeAl$_3$N$_5$]:Eu$^{2+}$ ($x = 0–2$)

Eugenia Elzer,[a] Philipp Strobel,[b] Volker Weiler,[b] Muhammad R. Amin,[c] Peter J. Schmidt,[b] Alexander Moewes,[c] and Wolfgang Schnick*[a]

Abstract: The nitridoberylloaluminate Ba$_2$[BeAl$_3$N$_5$]:Eu$^{2+}$ and solid solutions Sr$_x$Ba$_{2-x}$[BeAl$_3$N$_5$]:Eu$^{2+}$ ($x = 0.5, 1.0, 1.5$) were synthesized in a hot isostatic press (HIP) under 50 MPa N$_2$ atmosphere at 1200°C. Ba$_2$[BeAl$_3$N$_5$]:Eu$^{2+}$ crystallizes in triclinic space group $P$1 (no. 2) ($Z = 2$, $a = 6.1869(10)$, $b = 7.1736(13)$, $c = 8.0391(14)$ Å, $\alpha = 102.754(8)$, $\beta = 112.032(6)$, $\gamma = 104.765(7)$), which was determined from single-crystal X-ray diffraction data. The lattice parameters of the solid solution series have been obtained from Rietveld refinements and show a nearly linear dependence on the atomic ratio Sr:Ba. The electronic properties and the band gaps of $M_x$[BeAl$_3$N$_5$] ($M = $ Sr, Ba) have been investigated by a combination of soft X-ray spectroscopy and density functional theory (DFT) calculations. Upon irradiation with blue light (440–450 nm), the nitridoberylloaluminates exhibit intense orange to red luminescence, which can be tuned between 610 and 656 nm (fwhm$ = $ 1922–2025 cm$^{-1}$ (72–87 nm)). In contrast to the usual trend, the substitution of the smaller Sr$^{2+}$ by larger Ba$^{2+}$ leads to an inverse-tunable luminescence to higher wavelengths. Low-temperature luminescence measurements have been performed to exclude anomalous emission.

Introduction

In recent years, the constant search for new phosphors pushed solid-state lighting, based on light-emitting diodes (LEDs), to one of the most popular lighting solutions. Especially, further improving luminous efficacy of white phosphor-converted (pc) LEDs with high color rendition depends on phosphor materials with optimized luminescence properties.[1] The combination of a high color rendering index without compromising luminous efficacy is a key factor in the optimization of pc-LEDs.[2] Here, particularly the emission maximum and the width of the emission band of the red-emitting phosphor play a significant role to avoid emission in the deep red spectral area.

In this context, Eu$^{2+}$ doped nitrides are intensively investigated, as they do not only show good thermal and chemical stability, but also promising optical properties.[3] The luminescence observed in Eu$^{2+}$ activated phosphors can be generally attributed to transitions between the $4f^7(F)5d^1$ exited state and the $4f^7(S_{5/2})$ ground state and is highly sensitive towards the local environment of the activator ion.[4] Red-emitting nitrides like (Sr,Ba)$_2$Si$_2$N$_5$:Eu$^{2+}$[5] or (Ca,Sr)AlSiN$_3$:Eu$^{2+}$[6] already found their way into commercial application as phosphors in pc-LEDs, due to their excellent photoluminescence properties. However, since both compounds exhibit rather broad emission bands, the luminous efficacy is limited due to spill-over to the infrared region. Structures based on highly condensed anionic networks are shown to be beneficial for narrow-band emission.

The degree of condensation $\kappa$ is defined as the ratio of tetrahedral centers $T$ to coordinating N atoms ($\kappa = n(T)n(N)$). In theory $\kappa$ can be increased by replacing higher charged tetrahedral centers (Al$^{4+}$, Si$^{4+}$) with lower charged ones like Li$^{+}$ or Mg$^{2+}$. Indeed, these substitutions led to the discovery of promising narrow-band red-emitting phosphors, such as Sr[LiAl$_2$N$_5$]:Eu$^{2+}$ (SLA),[7] Sr[Mg$_2$Si$_3$N$_9$]:Eu$^{2+}$ (SMS),[8] or Sr[Li$_2$Al$_2$O$_4$N$_3$]:Eu$^{2+}$ (SALON).[9] Even though SMS exhibits an emission maximum in the desired spectral region at $\lambda_{\text{max}} = $ 615 nm and a very narrow emission band with a full width at half-maximum (fwhm) of 43 nm/1170 cm$^{-1}$, high thermal quenching prevents its application in pc-LEDs. SLA ($\lambda_{\text{max}} = 654$ nm, fwhm = 50 nm/1180 cm$^{-1}$) and the recently reported SALON ($\lambda_{\text{max}} = 614$ nm, fwhm = 48 nm/1286 cm$^{-1}$) show better thermal performance, but emission band widths of both...
In this contribution, we report on optical luminescence of $\text{Ba}_x[\text{BeAl}_2\text{N}_3]\text{Eu}^{2+}$ and the solid solution series $\text{Sr}_x\text{Ba}_y[\text{BeAl}_2\text{N}_3]\text{Eu}^{2+}$ ($x = 0.5, 1.0, 1.5$), as well as their syntheses and electronic properties. Upon irradiation with blue light, the nitridoberylloluminates exhibit intense orange to red luminescence. In contrast to the usual trend, the emission maximum in the nitridoberylloluminates $\text{Sr}_x\text{Ba}_y[\text{BeAl}_2\text{N}_3]\text{Eu}^{2+}$ ($x > 0$) is inversely shifted to higher wavelengths by the incorporation of the larger cation $\text{Ba}^{2+}$. This contribution shows that even small changes in the local environment in the investigated nitridoberylloluminates have a significant effect on the luminescence, since activator concentration and anomalous emission can be ruled out as causes for the unexpected, red-shifted emission with increasing size of the alkaline earth element.

## Results and Discussion

### Synthesis and chemical analysis

A modification of the reported synthesis for $\text{Sr}_x[\text{BeAl}_2\text{N}_3]\text{Eu}^{2+}$ gave access to a solid solution series with the nominal composition $\text{Sr}_x\text{Ba}_y[\text{BeAl}_2\text{N}_3]\text{Eu}^{2+}$ ($x = 0.5, 1.0$ and $1.5$) and $\text{Ba}_x[\text{BeAl}_2\text{N}_3]\text{Eu}^{2+}$. The products were obtained as crystalline powders with orange body color and red luminescence upon irradiation with blue light. The morphology of the crystals is shown in Figure S2. The atomic ratio of $\text{Sr}:\text{Ba}:\text{Al}:\text{N}$ (Table 1), as obtained from EDX measurements, range within the estimated standard deviations from the intended sum formulas for the solid solution series $\text{Sr}_x\text{Ba}_y[\text{BeAl}_2\text{N}_3]\text{Eu}^{2+}$.

Beryllium usually cannot be detected with this method. The oxygen content is insignificant within the estimated standard deviations and was only detected for the $\text{Sr}$-rich representatives of the solid solution series ($x = 0.5, 1.0$). A possible reason might be the hydrolysis sensitivity of the investigated powder samples. As already mentioned in the experimental section the formation of $\text{MBe}_2\text{N}_3$ ($\text{M} = \text{Sr}, \text{Ba}$ and $\text{SrO}$ as impurity phases hampered the preparation of a defined composition with regard to the atomic ratio of $\text{Sr}:\text{Ba}$ for the solid solution phases.

### Crystal structure

Based on the crystal structure solution and refinement (SHELX-2014), $\text{Ba}_x[\text{BeAl}_2\text{N}_3]\text{Eu}^{2+}$ crystallizes in space group $\text{P1}$ (no. 2).

### Table 1. EDX results of $\text{Sr}_x\text{Ba}_y[\text{BeAl}_2\text{N}_3]\text{Eu}^{2+}$ ($x = 0.0, 0.5, 1.0, 1.5, 2.0$).

| $x$ | 0   | 0.5 | 1.0 | 1.5 | 2.0 |
|-----|-----|-----|-----|-----|-----|
| th. | exp | th. | exp | th. | exp |

| $\text{Sr}_x\text{Ba}_y[\text{BeAl}_2\text{N}_3]\text{Eu}^{2+}$ |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $\text{Sr}$ | 20  | 25(3) | 15 | 11(3) | 10 | 9(1) | 5 | S(1) | 0 | 0 |
| $\text{Ba}$ | 0   | 0   | S(2) | 10 | 12(2) | 15 | 14(1) | 20 | 16(3) | 30 |
| $\text{Al}$ | 30  | 30(4) | 30 | 32(4) | 30 | 34(3) | 30 | 33(2) | 30 | 36(2) |
| $\text{N}$ | 50  | 45(6) | 50 | 43(4) | 50 | 44(3) | 50 | 48(3) | 50 | 49(3) |
| $\text{O}$ | 0   | 0   | 7(7) | 0 | 1(1) | 0 | 0 | 0 | 0 | 0 |
isotypical to Sr$_2$[BeAl,N$_3$]:Eu$^{2+}$. During the refinement of the crystal structure the small amount of Eu$^{2+}$ was neglected, due to the insignificant contribution to the scattering density. Crystallographic data of the Ba-containing phase show an increase of the unit cell volume (~7%) compared to Sr$_2$[BeAl,N$_3$]:Eu$^{2+}$, due to the incorporation of the larger Ba$^{2+}$ ion (Table 2).

Detailed crystallographic data, atomic coordinates, Wyckoff positions, isotropic displacement parameters, anisotropic displacement parameters and selected distances and angles of Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ are summarized in the Supporting Information (Tables S3–S7). Detailed information on the single-crystal data of Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service. Deposition Number CSD-2121521 (for Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$) contains the supplementary crystallographic data for this paper.

The crystal structure of Ba$_3$[BeAl,N$_3$]:Eu$^{2+}$ (Figure 1a) consists of edge- and vertex-sharing AlN$_5$ tetrahedra and trigonal-planar BeN$_3$ units. Each AlN$_5$ tetrahedron shares one edge with another AlN$_5$ tetrahedron building a bow-tie unit ([Al,N$_5$]$^{1-}$) and each BeN$_3$ unit is connected to a second BeN$_3$ unit over a common edge, building a planar [Be,N$_3$]$^{3-}$ unit (Figure 1b). These building units are further connected by common vertices forming a three-dimensional anionic network, which contains channels filled with Ba$^{2+}$ (and Eu$^{2+}$, when doped) for charge neutrality. The alkaline earth (AE) ions are distributed over three different coordination sites (Ba1, Ba2 and Ba3) and coordinated by seven (Ba1) and eight (Ba2 and Ba3) N atoms, respectively (Figure 1c).

The interatomic distances between Ba atoms and N atoms are in the range of 2.719(5)–3.243(4) Å, which is comparable with other Ba-containing nitrides with a coordination number (CN) of eight (Figure S3). The increase of the distances in the sequence $d_{Ba1-N} < d_{Ba2-N} < d_{Ba3-N}$ corresponds well with the higher CN around Ba2 and Ba3. Both effects explain the increased thermal displacements of the Ba2/Ba3 sites in comparison to Ba1 (Table S5). The different distances are also reflected in the polyhedral volumes, which are significantly smaller around Ba1 (31.64 Å$^3$) relative to Ba2 (46.15 Å$^3$) and Ba3 (44.41 Å$^3$).

The bulk phase composition of the samples was determined by Rietveld refinement of powder X-ray diffraction data (Table S8). For the refinement of Sr$_2$-Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ ($x > 0$), the structural model of Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ from single-crystal X-ray diffraction data was used. Representative for all samples, the plot of the Rietveld refinement of Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ is shown in Figure 2, confirming Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ as the main phase.

The sample contains small amounts of AlN and BaBe$_2$N$_3$ as impurity phases. Rietveld refinement plots for Sr$_2$-Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ ($x > 0$) are provided in the Supporting Information (Figure S4).

Due to the larger ionic radius of Ba$^{2+}$ compared to Sr$^{2+}$, the lattice parameters of the samples are increasing with Ba$^{2+}$ partially or completely occupying the Sr sites. Comparing the lattice parameters (Figure 3), an almost linear dependence on the atomic ratio Ba: Sr is observed.

As already discussed above, the structure provides three crystallographically independent AE$^{2+}$ (AE$^{2+}$ = Sr, Ba) sites (Figure 1c) with coordination polyhedra of different sizes and shapes. Since the local coordination around the cation replaced by Eu$^{2+}$ can have a strong influence on the photoluminescence properties of the nitridoberylloaluminates, the occupation of Sr/Ba1, Sr/Ba2 and Sr/Ba3 sites was investigated using Rietveld refinements. A graphical representation of the site occupation

---

**Table 2.** Crystallographic data of Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ compared to reported values for Sr$_2$[BeAl,N$_3$]:Eu$^{2+}$. Standard deviations in parentheses.

|                | Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ | Sr$_2$[BeAl,N$_3$]:Eu$^{2+}$ |
|----------------|-----------------------------|-----------------------------|
| Formula mass /g mol$^{-1}$ | 343.68                      | 335.24                      |
| Crystal system | triclinic                   | triclinic                   |
| Space group    | P1 (no. 2)                  | P1 (no. 2)                  |
| Cell parameter /Å$^{-1}$ |                             |                             |
| $a$           | 6.061(2)                    | 6.1869(10)                  |
| $b$           | 6.982(3)                    | 7.1736(13)                  |
| $c$           | 7.872(4)                    | 8.0391(14)                  |
| $a$           | 102.22(3)                   | 102.754(8)                  |
| $c$           | 112.62(2)                   | 112.032(6)                  |
| $\gamma$     | 104.02(2)                   | 104.765(7)                  |
| Volume/Å$^3$  | 280.5(2)                    | 280.5(2)                    |
| X-ray density/g cm$^{-3}$ | 3.969                       | 4.824                       |

---

**Figure 1.** Crystal structure representation of Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ with Al atoms (light blue), Be atoms (green), N atoms (blue) and Ba atoms (gray). a) view of 2 x 2 x 2 unit cells along [001]; b) bow-tie unit [Al,N$_5$]$^{1-}$ (top, light blue) and [Be,N$_3$]$^{3-}$ unit (bottom, green); c) coordination polyhedra (gray) around Ba1 (top), Ba2 (middle) and Ba3 (bottom).

**Figure 2.** Rietveld refinement of Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ (Mo $\lambda_{\text{K}α} = 0.71073$ Å). Experimental data (black line), calculated pattern (red line) and difference curve (gray line). Tick marks: position of Bragg reflections of Ba$_2$[BeAl,N$_3$]:Eu$^{2+}$ (green), AlN (blue), and BaBe$_2$N$_3$ (orange).
Electronic properties

The electronic properties of $M_x[\text{BeAl}_3\text{N}_2]\text{Eu}^{2+}$ ($M=$Sr, Ba) were investigated by a combination of synchrotron-based soft X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES), as well as DFT calculations. As the results for both compounds are quite similar, the XES, XAS, resonant inelastic X-ray scattering spectra (RIXS) and a non-resonant X-ray emission spectrum (NXES) for $\text{Sr}_x[\text{BeAl}_3\text{N}_2]\text{Eu}^{2+}$ are shown in Figure 5, while the spectra for $\text{Ba}_x[\text{BeAl}_3\text{N}_2]\text{Eu}^{2+}$ can be found in the Supporting Information (Figure S5). The solid black line shown in Figure 5b corresponds to the experimental PFY for $\text{Sr}_x[\text{BeAl}_3\text{N}_2]\text{Eu}^{2+}$, which is compared to core hole (solid orange line) and ground state (dash-dotted orange line) calculations. It is found that the experimental XAS spectrum is in good agreement with the core hole calculations, as all major features are reproduced at the correct energy positions and approximately at the correct peak heights. The comparison of the two calculated absorption spectra (Figure 5b, orange) to the measured spectrum (Figure 5b, black) makes it clear that the core hole concentration in the experiment lies somewhere between the two calculated cases. Therefore, the core hole concentration should be more dilute than the case we calculated, and which reflects 1 of 20 atoms in the supercell missing a 1s electron. A more diluted core hole concentration (and hence larger supercell) was computationally not feasible due to the increased cpu time that would be required.

Figure 3. Comparison of the lattice parameters $a$ (red), $b$ (black), and $c$ (light blue), and the volume of the unit cell $V$ (green) of $\text{Sr}_{x-}\text{Ba}_x[\text{BeAl}_3\text{N}_2]\text{Eu}^{2+}$ with $x=0, 0.5, 1.0, 1.5$ and 2.0 obtained from Rietveld refinements.

Figure 4. Graphical representation of the site occupation factors of the three crystallographic sites occupied by Sr and/or Ba in the solid solution series $\text{Sr}_{x-}\text{Ba}_x[\text{BeAl}_3\text{N}_2]\text{Eu}^{2+}$. Wyckoff positions of the respective sites are given in brackets. The darker color represents Sr, while the lighter color stands for Ba.

Figure 5. Experimental and calculated N K-edge XES and XAS spectra of $\text{Sr}_x[\text{BeAl}_3\text{N}_2]\text{Eu}^{2+}$: a) NXES spectrum (black) excited at 440.0 eV and RIXS spectra (red, magenta, and blue) collected at 398.3 eV, 399.8 eV, and 401.2 eV are compared with ground state calculations (orange). The vertical dotted magenta line indicates that the highest emission energy is observed at the highest excitation energy in the RIXS spectra, which indicates an indirect band gap; b) Comparison of experimental PFY (black), core hole (CH) and ground state (GS) calculations of N K-edge XAS spectra. The small color coded arrows in the embedded figure indicate where in the conduction band (CB) the N 1s electron was excited to obtain the emission spectra of the corresponding color; c) Second derivative of the NXES spectrum, with peaks that are above the noise level and are corresponding to the valence band edge indicated by the arrow; d) Second derivative of PFY of XAS spectrum with peaks corresponding to CB edge indicated by the arrow.

The refinement was restrained to allow only electroneutral sum formula. Therefore, the three crystallographic sites were assumed to be fully occupied while the Sr:Ba ratio was refined. According to the refinements, the atomic ratios of Sr:Ba are 1.3:0.7 ($x=0.5$), 1.1:0.9 ($x=1.0$) and 0.7:1.3 ($x=1.5$).

Due to the different ionic radii of Ba$^{2+}$ (1.26 Å, CN = 8) and Sr$^{2+}$ (1.42 Å, CN = 8), an ordering of the heavy atoms is plausible. The members of the solid solution, however, do not show ordering of the AE$^{2+}$ ions, but indicate a mixed occupancy of all three sites (Figure 4). But the distribution of the larger polyhedral volumes compared to the Sr/Ba$^1$ site. The impact of these results will be further discussed in the luminescence section.

It is found that the experimental XAS spectrum is in good agreement with the core hole calculations, as all major features are reproduced at the correct energy positions and approximately at the correct peak heights. The comparison of the two calculated absorption spectra (Figure 5b, orange) to the measured spectrum (Figure 5b, black) makes it clear that the core hole concentration in the experiment lies somewhere between the two calculated cases. Therefore, the core hole concentration should be more dilute than the case we calculated, and which reflects 1 of 20 atoms in the supercell missing a 1s electron. A more diluted core hole concentration (and hence larger supercell) was computationally not feasible due to the increased cpu time that would be required.
As the absorption and emission spectra are proportional to the unoccupied and occupied pDOS, respectively their separation can be used to determine the electronic band gap, using the second derivative method. Here, the valence band (VB) and the conduction band (CB) edges are taken to be the first peaks in the DOS (Figure 5 and Figure S5) the estimated band gap is found to be 3.4 ± 0.3 eV for Sr,[BeAl,N₂]₂Eu⁺⁺ and 3.1 ± 0.3 eV for Ba,[BeAl,N₂]₂Eu⁺⁺, respectively. This result must be adjusted to account for the effect of the N 1s core hole that is created during the excitation process. Applying a DFT-derived correction of 0.1 eV the final experimental band gaps are found to be 3.5 ± 0.3 eV (M = Sr) and 3.2 ± 0.3 eV (M = Ba), respectively. The calculated band gap using PBE-GGA is found to be 2.8 eV (M = Sr) and 2.56 eV (M = Ba), respectively. This underestimation is typical for DFT and can be improved by using the modified Becke-Johnson (mBJ) exchange-correlation potential.[21] In this case, the calculated band gaps are found to be 4.2 eV (M = Sr) and 3.6 eV (M = Ba). A summary of the band gap values can be found in Table 3.

The band structure of M,[BeAl,N₂]₂Eu⁺⁺ (M = Sr, Ba) was calculated using the mBJ exchange-correlation potentials (Figure S6). The calculations indicate an indirect band gap for both materials with the valence band (VB) maximum at the T point for both compounds and the conduction band (CB) minimum at the I point for Sr,[BeAl,N₂]₂Eu⁺⁺ and Z point for Ba,[BeAl,N₂]₂Eu⁺⁺, respectively. The pDOS of both compounds (Figure S7) show high similarity with other materials based on XN₄ (X = Li, Al, Mg, Si) tetrahedra, for example, SLA,[22] Li₂Ca,[Mg,Si,N₂]₂Eu⁺⁺[23] or BaLi,[Al,Si,N₂]₂Eu⁺⁺[23] where the upper VB is dominated by N p states and the lower VB is characterized by X s/p states. Meanwhile, the alkaline earth ion d states strongly contribute to the lower CB. Based on the definition of Dorenbos, there are two types of compounds: type I compounds, where the bottom of the CB is dominated by alkaline earth ions which are replaced by rare earth ions, and type II compounds, where the lower CB is dominated by ions that are not replaced by the rare earth ion.[24] Typically, type I compounds show an increasing band gap with smaller size of the alkaline earth, which is in accordance with the values obtained for M,[BeAl,N₂]₂Eu⁺⁺ (M = Sr, Ba), where Sr-containing phosphor show larger band gap values (Table 3).

UV-vis spectroscopy

Additionally, the optical band gaps of Sr,[BeAl,N₂]₂Eu⁺⁺ and Ba,[BeAl,N₂]₂Eu⁺⁺ were estimated from reflectance data and compared to the ones obtained from XAS/XES experiments and DFT calculations. The reflectance spectra R were converted to pseudosorption spectra using the Kubelka-Munk function \( F(R) = (1 - R)^2/(2R) \) (Figure S8).[25] The optical band gaps were determined through a linear fit of the data at the inflection point from the Tauc plots (\( F(R)h\nu \)) with \( n = 1/2 \) for a direct and \( n = 2 \) for an indirect allowed transition for a better comparison with the literature (direct band gap for Sr,[BeAl,N₂]₂Eu⁺⁺ of 3.8 eV).[13] The values are summarized in Table 3 and are approximately in the same range, as the calculated (GGA and mBJ) and experimentally (XES/XAS) determined band gaps.

Luminescence

Luminescence measurements were carried out on samples with various compositions. Excitation and emission spectra of single particles of the solid solution series SrₓBa₁₋ₓ[BeAl,N₂]₂Eu⁺⁺ (x = 2.0) are displayed in Figure 6 (2 mol% Eu⁺⁺ concentration referred to Sr/Ba).

The excitation spectra in Figure 6a show that all members containing nitridoberylloaluminate, Ba,[BeAl,N₂]₂Eu⁺⁺ exhibits a red-shifted emission maximum at \( \lambda_{\text{em}} = 656 \text{ nm} \) with a fwhm of \( \approx 87 \text{ nm}/2025 \text{ cm}^{-1} \). The position of the emission maximum and the shape of the emission band obtained from single particles are comparable to those obtained from bulk samples (Supporting Information, Figure S10). Therefore, the luminescence properties of the bulk samples can be assigned to Ba,[BeAl,N₂]₂Eu⁺⁺ and rules out a possible contribution to the red emission by the side phase BaBe₄N₅. The value of the
internal quantum efficiency (IQE) at room temperature for \( \text{Ba}_2[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \) is 44%, which is similar to \( \text{Sr}_2[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \) (33%). Overall, the photoluminescence properties of \( \text{Ba}_2[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \) are comparable to other nitrides, some of which are summarized in Table 4.

To investigate the effect of the substitution of \( \text{Sr}^{2+} \) with \( \text{Ba}^{2+} \) on the \( \text{Eu}^{2+} \) luminescence in \( \text{Sr}_2 \cdot \text{Ba}_x[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \), luminescence emission spectra of samples with \( x = 0, 0.5, 1.0, 1.5 \) and 2.0 were measured (Figure 6b). The emission maxima obtained from samples of the solid solution series show tunable emission between 610 to 656 nm through the compositional variable \( x \) (Figure 7).

The fwhm values for \( x = 0 \) (72 nm/1922 cm\(^{-1}\)) and \( x = 2 \) (87 nm/2025 cm\(^{-1}\)) are slightly smaller with values around 2000 cm\(^{-1}\), while in \( \text{Sr}_2 \cdot \text{Ba}_x[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \) with \( x = 0.5, 1.0 \) and 1.5 the fwhm is increased up to 2200 cm\(^{-1}\). The fwhm broadening is caused by varying \( \text{Eu}-\text{N} \) distances, resulting from mixed occupation of the three alkaline earth sites as discussed in the crystal structure section. Furthermore, in the samples with mixed occupation of the \( \text{Sr}/\text{Ba} \) sites, a second emission maximum occurs at shorter wavelengths, peaking around 550 nm. The intensity of this second emission maximum is very weak and almost identical for the samples with \( x = 0.5 \) and 1.0 and decreases even further in the sample with \( x = 1.5 \).

Comparing the low-temperature measurements of \( \text{Sr}_2[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \) and \( \text{Ba}_2[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \) (Figure S10) only one broad emission band is observed for the \( \text{Ba} \) compound, while the superposition of three emission maxima is observed at 6 K for \( \text{Sr}_2[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \). In the mixed phases, it can be observed that this second emission maximum also decreases in intensity as the \( \text{Sr} \) content of the compound decreases. Therefore, the assumption is that this emission maximum originates from \( \text{Eu}^{2+} \) on the \( \text{Sr}/\text{Ba1} \) site which contains the highest \( \text{Sr} \) content according to the Rietveld refinement (Figure 4).

Cationic substitution is often used to alter the emission color of nitride phosphors, as the emission is strongly influenced by the local environment around the activator \( \text{Eu}^{2+} \). Generally, the substitution of a smaller ion by a bigger one should lead to a smaller crystal field splitting and therefore shifting the emission color to shorter wavelengths.[3] Contrary to such observations, the emission of the solid solution series \( \text{Sr}_2 \cdot \text{Ba}_x[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \) is inversely shifted from 610 towards 656 nm with increasing \( \text{Ba} \) content as illustrated in Figure 7. The small leap in the position of the emission maximum observed between \( x = 0 \) and \( x = 0.5 \) is consistent with the interval observed analyzing the lattice parameter dependence on the \( \text{Ba}/\text{Sr} \) ratio, displayed in Figure 3.

Possible reasons for the uncommon, inverse-tunable red emission of \( \text{Sr}_2 \cdot \text{Ba}_x[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \) will be discussed in the following section. Such a red-shifted emission can be associated with the activator concentration, the occurrence of anomalous trapped exciton emission or occur due to a change in the local environment around \( \text{Eu}^{2+} \) without necessarily changing the crystal structure of the compound.[17a,28]

In crystal structures with multiple crystallographic sites for the incorporation of the activator, the activator can act as donor and acceptor, enabling energy transfer between the activator ions. Typically, the probability for an energy transfer depends on the distance between the \( \text{Eu}^{2+} \) atoms, therefore a red-shift of the emission with increasing activator concentration can take place, as already observed in different phosphors (for example, \( M_5\text{Si}_4\text{N}_2\text{Eu}^{2+} \) \( (M = \text{Sr}, \text{Ba}) \) [28a,29] or \( \text{Ca}_5\text{Eu}_3\text{SiO}_4 \) [30]). Luminescence spectra of bulk samples of \( \text{Ba}_x[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \) with a nominal \( \text{Eu}^{2+} \) concentration of 0.3, 1, 2, 3, and 4 mol% referred to \( \text{Ba} \) are shown in the Supporting Information (Figure S9) and were compared with the reported spectra for \( \text{Sr}_2[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \) [31].

In the literature, it has been reported that the location of the emission maximum does not change as the \( \text{Eu} \) content increases for \( \text{Sr}_2[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \). A comparable behavior was observed for \( \text{Ba}_2[\text{BeAl}_2\text{N}_2] \cdot \text{Eu}^{2+} \). Phase-pure samples will be necessary to further investigate luminescence properties in even more detail. Based on the current data, a red-shift of the emission due to increasing activator concentrations seems to be rather unlikely.

As anomalous trapped exciton emission is known to occur more likely in phosphors with \( \text{Eu}^{2+} \) on sites with high coordination number and large activator-ligand bond lengths,[28d] temperature-dependent emission measurements were performed to investigate the luminescence properties of the title compounds at lower temperatures (Figures S10–S12). The obtained spectra show no significant shift of the emission maxima at lower temperatures, suggesting that anomalous emission is an unlikely explanation for the unusual inverse shift of the emission maxima to higher wavelengths.
The third option to discuss is the dependence of the emission on structurally related properties, especially of Eu\(^{2+}\) states influenced by its surrounding ligands. As already stated in the introduction, the 4f-5d transition, which defines the excitation and emission properties of Eu\(^{2+}\) doped phosphors, is highly sensitive toward the local coordination environment around the activation ion. When Eu\(^{2+}\) replaces Sr\(^{2+}\) in Sr\(_2\)(BeAl\(_4\))N\(_2\):Eu\(^{2+}\), no structural changes are expected, as the ionic radii of both ions are quite similar [Eu\(^{2+}\) : 1.25 Å (CN = 8) and 1.20 Å (CN = 7); Sr\(^{2+}\) : 1.26 Å (CN = 8) and 1.21 Å (CN = 7)].\(^{[26]}\) The situation is quite different with Ba\(^{2+}\), as the ionic radius is larger than that of Eu\(^{2+}\) [Ba\(^{2+}\) : 1.42 Å (CN = 8) and 1.38 Å (CN = 7)].\(^{[20]}\) Therefore, incorporation of Eu\(^{2+}\) on a larger crystallographic site can lead to red-shifted emission due to local lattice rearrangement. Considering the stepwise substitution of the lighter alkaline earth ion by the heavier homologue in the solid solution series, the activator Eu\(^{2+}\) preferentially replaces Sr atoms due to the similar ionic radii. When the neighboring Sr atoms are gradually replaced by the larger Ba\(^{2+}\), the strain in the Ba–N bond distances increases leading to shorter Sr–N and Eu–N bond lengths, in order to release lattice strain. The more Sr atoms are replaced by Ba\(^{2+}\), the shorter the Eu–N and Sr–N distances become. Shorter activator-ligand distances increase the crystal field splitting of the 5d orbitals resulting in a broadening of the emission band, which is comparable to other narrow-band red-emitting phosphors like Sr\(_2\)(LiAl\(_4\))N\(_2\):Eu\(^{2+}\), the members of the solid solution series show much broader emission bands, most probably due to the convolution of the emission from three different coordinated Eu\(^{2+}\) sites. In contrast to the usual trend, the emission maximum in the nitridoberylloaluminates Sr\(_2\)Ba\(_x\)(BeAl\(_4\))N\(_2\):Eu\(^{2+}\) (x = 0–2) is inversely shifted to higher wavelengths by increasing the Ba content. This fact emphasizes the importance of studies regarding the structures and properties of potential phosphors, since the Eu\(^{2+}\) emission can be significantly influenced by small local changes and distortions of the environment without necessarily changing the symmetry of the crystal.

In summary, the synthesis of the presented compounds and the study of their electronic and optical properties contributes to the elucidation of the so far little explored class of nitridoberylloaluminates and emphasizes their role in the discovery and development of new luminescent materials.

### Acknowledgements

The authors thank Karl Adriaan Zijtveld (Lumileds Phosphor Center Aachen) for luminescence measurements, Dr. Christian Maak and Christian Minke for EDX measurements and Dr. Peter Mayer (all Department of Chemistry, University of Munich (LMU)) for collecting single-crystal X-ray diffraction data. The soft X-ray spectroscopy measurements were performed at the Canadian Light Source (CLS), which is funded by the Canada Foundation for Innovation, the Natural Science and Engineering Research Council of Canada (NSERC), the National Research Council Canada, the Canadian Institutes of Health Research, the Government of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan. The authors also acknowledge Compute Canada. The calculations presented in this paper were performed on the Cedar high-performance computing cluster, which is part of the WestGrid (www.westgrid.ca) and Compute Canada Calcul Canada (www.computecanada.ca). Open Access funding enabled and organized by Projekt DEAL.

### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** aluminium · beryllium · luminescence · nitrides · X-ray absorption spectroscopy
[1] M. Pattison, M. Hansen, N. Barsdley, C. Elliott, K. Lee, L. Pattison, J. Tsao, Office of Scientific and Technical Information (OSTI), 2020.
[2] J. L. Leaño, M.-H. Fang, R.-S. Liu, ECS J. Solid State Sci. Technol. 2017, 7, R3111–R3133.
[3] L. Wang, R. J. Xie, T. Suehiro, T. Takeda, N. Hirotsu, Chem. Rev. 2018, 118, 1951–2009.
[4] A. Meierink, G. Blasse, J. Lumin. 1989, 43, 283–289.
[5] R.-J. Xie, N. Hirotsu, T. Suehiro, F.-F. Xu, M. Mitomo, Chem. Mater. 2006, 18, 5578–5583.
[6] H. Watanabe, N. Kijima, J. Alloys Compd. 2009, 475, 434–439.
[7] P. Pust, V. Weiler, C. Hecht, A. Tucks, A. S. Wochnik, A. K. Henss, D. Wiechert, C. Schau, P. J. Schmidt, W. Schnick, Nat. Mater. 2014, 13, 891–896.
[8] S. Schmietien, H. Schneider, P. Wagatha, C. Hecht, P. J. Schmidt, W. Schnick, Chem. Mater. 2014, 26, 2712–2719.
[9] G. J. Hoerder, M. Seibald, D. Baumann, T. Schroder, S. Peschke, P. C. Schmid, T. Tyborski, P. Pust, I. Stoll, M. Bergler, C. Patsig, S. Reissaus, M. Krause, L. Berthold, T. Hoche, D. Johrendt, H. Huppertz, Nat. Commun. 2019, 10, 1–9.
[10] P. Strobel, T. de Boer, V. Weiler, P. J. Schmidt, A. Moewes, W. Schnick, Chem. Mater. 2018, 30, 3122–3130.
[11] P. Strobel, C. Maak, V. Weiler, P. J. Schmidt, W. Schnick, Angew. Chem. Int. Ed. 2018, 57, 8739–8743; Angew. Chem. 2018, 130, 8875–8879.
[12] E. Elzer, R. Niklaus, P. J. Strobel, V. Weiler, P. J. Schmidt, W. Schnick, Chem. Mater. 2019, 31, 3174–3182.
[13] E. Elzer, P. Strobel, V. Weiler, P. J. Schmidt, W. Schnick, Chem. Mater. 2020, 32, 6611–6617.
[14] S. Schmietien, P. Strobel, C. Hecht, T. Reith, M. Siegert, P. J. Schmidt, P. Huppertz, D. Wiechert, W. Schnick, Chem. Mater. 2015, 27, 1780–1785.
[15] P. Pust, F. Hintze, C. Hecht, V. Weiler, A. Locher, D. Zitnanska, S. Harm, D. Wiechert, P. J. Schmidt, W. Schnick, Chem. Mater. 2014, 26, 6113–6119.
[16] P. Strobel, V. Weiler, P. J. Schmidt, W. Schnick, Chem. Eur. J. 2018, 24, 7243–7249.
[17] a) P. Dorenbos, J. Phys. Condens. Matter 2003, 15, 2645–2665; b) J. L. Sommerdijk, A. Brl, J. Lumin. 1976, 11, 363–367.
[18] a) M. Zhao, Q. Zhang, Z. X. Acc. Mater. Res. 2020, 1, 137–145; b) Y. Zhuo, A. Mansouri Tehrani, A.-O. Olynyk, A. C. Duke, J. Briscoe, Nat. Commun. 2018, 9, 1–10; c) N. Hirotsu, T. Takeda, S. Funahashi, R.-J. Xie, Chem. Mater. 2014, 26, 4280–4288; d) X. Zhou, J. Qiao, Z. Xia, Chem. Mater. 2021, 33, 1083–1098.
[19] G. M. Sheldrick, Acta Crystallogr. Sect. C 2015, 71, 3–8.
[20] R. D. Shannon, Acta Crystallogr. Sect. A 1976, 32, 751–767.
[21] F. Tran, P. Blaha, Phys. Rev. Lett. 2009, 102, 226401.
[22] T. M. Tolhurst, T. D. Boyko, P. Pust, N. W. Johnson, W. Schnick, A. Moewes, Adv. Opt. Mater. 2015, 3, 546–550.
[23] T. M. Tolhurst, P. Strobel, P. J. Schmidt, W. Schnick, A. Moewes, J. Phys. Chem. C 2017, 121, 14296–14301.
[24] P. Dorenbos, J. Phys. Condens. Matter 2005, 17, s1031–s111.
[25] a) R. López, R. Gómez, J. Sol-Gel Sci. Technol. 2012, 61, 1–7; b) J. Tauc, R. Grigorovici, A. Vancu, Phys. Status Solidi B 1966, 15, 627–637; c) P. Kubelka, J. Opt. Soc. Am. 1948, 38, 448–457.
[26] P. Wagatha, V. Weiler, P. J. Schmidt, W. Schnick, Chem. Mater. 2018, 30, 1755–1761.
[27] D. Wilhelm, D. Baumann, M. Seibald, K. Wurst, G. Heymann, H. Huppertz, Chem. Mater. 2017, 29, 1204–1209.
[28] a) Y. Qi, L. J. E. van Steen, J. W. H. van Krevel, G. Botty, A. C. A. Delsing, F. J. DiSalvo, G. de With, H. T. Hintzen, J. Alloys Compd. 2006, 417, 273–279; b) G. Li, C. C. Lin, W.-T. Chen, M. S. Molokeev, V. V. Atuchin, C.-Y. Chiang, W. Zhou, C.-W. Wang, W.-H. Li, H.-S. Sheu, T.-S. Chan, C.-M. Liu, Chem. Mater. 2014, 26, 2991–3001; c) J. L. Leano, Jr., C. O. M. Mariano, W. T. Huang, S. Mahlik, T. Lesniewski, M. Grinberg, H. S. Sheu, S. F. Hu, R. S. Liu, ACS Appl. Mater. Interfaces 2020, 12, 23165–23171; d) A. Lazarowska, S. Mahlik, M. Grinberg, C.-C. Lin, R. S. Liu, J. Phys. Chem. B 2015, 142, 134704.
[29] H. A. Hoppé, H. Lutz, P. Morys, W. Schnick, A. Seilmeyer, J. Phys. Chem. Solids 2000, 61, 2001–2006.
[30] Y. Sato, H. Kato, M. Kobayashi, T. Masaki, D. H. Yoon, M. Kakihana, Angew. Chem. Int. Ed. 2014, 53, 7756–7759; Angew. Chem. 2014, 30, 7890–7893.
[31] H. Watanabe, H. Wada, K. Seki, M. Itou, N. Kijima, J. Electrochem. Soc. 2008, 155, F31-F36.

Manuscript received: November 16, 2021
Accepted manuscript online: January 12, 2022
Version of record online: February 2, 2022