Novel red-emitting nitridoborates - $SrBa_8[BN_2]_6{:}Ln^{2+/3+}$ ($Ln = Pr^{3+}$, Eu^{2+})

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ABSTRACT

This work concerns the photoluminescence (PL) properties of the novel phosphors $SrBa_8[BN_2]_6{:}Ln^{2+/3+}$ ($Ln = Pr^{3+}$, Eu^{2+}). The presented samples were synthesized via a conventional solid-state route in a protective atmosphere and subsequently analysed with respect to their (phase) purity and photoluminescence properties. To this end, samples were combusted and the nitrogen and oxygen content was determined. PL measurements included temperature dependent excitation and emission spectra as well as the investigation of thermal luminescence, i. e. glow curves. Furthermore, decay constants were derived in order to clarify the origin of the PL of undoped materials and to illuminate the interplay between the activator luminescence and defect states.

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1. Introduction

The emergence of phosphor converted light emitting diodes (pcLED's) that rapidly replace outdated concepts for the generation of light, i.e. incandescent or fluorescent lamps, triggered intense research for new phosphors excitable by LED chips emitting in the violet or blue region of the electromagnetic spectrum. Current state-of-the-art LED chips consist of elaborated structured (Ga,In)N stacks [1–5] with emission wavelengths ranging from 370–500 nm, although it is not yet clear which peak wavelength will immerse as the most efficient one. By now, a number of efficient phosphors for the generation of white light—either cool, with correlated colour temperatures (CCT) > 4000 K, or warm with CCT < 4000 K—from LED's are known and applied in series production. The mostly applied material for cool white LED's is $(Lu,Y)_3Al_5O_{12}{:}Ce^{3+}$, which is excitable at 410–460 nm and emits in the green-yellow range of the electromagnetic spectrum. Such pcLED's exhibit high luminous efficacies (LE) due to the good overlap of the emission spectrum and the spectral sensitivity of the human eye. However, the drawback of high efficacies is a rather low colour rendering index (CRI) which means poor colour reproduction undesired for general lighting applications in living areas. Additional phosphors emitting in the red spectral range lower the efficiency of the LED but increase its CRI, which is why the urge for narrow red-emitting phosphors, providing

enhanced CRI with as little loss in efficiency as possible, is great.[6] At the moment, most commonly used red emitting phosphors are nitride based materials, e.g. $(Ca,Sr)AlSiN_3{:}Eu^{2+}$[7] or $(Sr,Ba)_2Si_5N_8{:}Eu^{2+}$,[8] while *Schnick* et al. recently reported on a material with an exceptionally narrow red emission band from Eu^{2+} in $Sr[LiAl_3N_4]{:}Eu^{2+}$[9].

In contrary to general lighting, phosphors applied in display illumination are mostly line emitters comprising for instance Eu^{3+} or Sm^{3+} in order to accomplish a wide colour gamut. However, these materials often suffer from poor excitability in the range where todays LED's emit. Although a number of efficient red-emitting phosphors already exist, all suffer from their own limitations, e.g. $K_2SiF_6{:}Mn^{4+}$,[10] proving the need for new classes of materials with superior physical and chemical properties.

One such material class hitherto neglected might be the field of nitridoborates. As *Gobeau* and *Anselment* reported on the first nitridoborates in the early 1960s,[11] they pioneered a rapidly expanding field of research. Since then, nitridoborates of alkali metals, alkaline earth metals and lanthanides have been reported. Many of them exhibit interesting structural and electronic features. For instance, lanthanides in combination with transition metals exhibit supra conductivity as in $La_3Ni_2[BN]_2N$[12] or are used as catalysts[13,14] to transform hexagonal boronitride into its cubic phase. Both materials are being used as highly stable functional materials themselves. Another interesting aspect of nitridoborate chemistry is the broad variability of the anion sublattice with N^{3-}, BN^{x-}, BN_2^{3-}, BN_3^{6-}, $B_2N_4^{8-}$, $B_3N_6^{9-}$ and even combinations thereof as possible

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structural elements. Also, oxo-nitridoborates with either O^{2-} or even BN_2O units have been reported.[15–17] It has also been shown that only partial substitution of nitrogen by oxygen is possible.[18,19] This leads, in theory, to a vast number of yet unknown compounds with promising properties.

Their use as phosphors has been investigated in some cases but activity in this field is still very low, most likely due to the difficulties linked to the synthesis and the stability of the final compounds.[20–24] Most known nitridoborates are sensitive to moisture and air with lanthanide nitridoborates and $Ca_2[BN_2]F$ being the exceptions. None the less, it is important to investigate their photoluminescence (PL) properties to gain insight into fundamental luminescence processes depending on the respective structural elements present in the material. This is why in this study we investigated (thermal) PL properties, reflectance spectra, and time dependent PL of $SrBa_8[BN_2]_6$ doped by divalent and trivalent luminescent activators.

2. Experimental

2.1. Synthesis

For the synthesis of polycrystalline samples of doped and undoped $(Sr_{1-x}Ln_x)Ba_8[BN_2]_6$ ($Ln=Pr^{3+}$, Eu^{2+}) with $0 \leq x \leq 0.05$, Sr_3N_2 (Materion, 99.7%), Ba_3N_2 (Materion, 99.6%), h-BN (Alfa Aesar, 99.5%), PrN (Pr_6O_{11}, Treibacher Industrie AG, 99.99%) and EuN in the appropriate atomic ratios were used as starting materials. LnN ($Ln=Pr$, Eu) was synthesized from the metals (Treibacher Industrie AG, 99.9% TREM) employing a synthesis route described elsewhere.[25] In case of the praseodymium doped samples, Pr_6O_{11} proofed to be a superior starting material over PrN. Educts were weighed and thoroughly blended in an agate mortar before being transferred into BN crucibles. Lidded crucibles were then fired at 1000 °C for 8 h in N_2/H_2 (10% H_2) (Westfalen AG, 5.0). Protective and reactive gases were purified by an "oxisorb"-cartridge, which reduces the oxygen and moisture levels below five and thirty parts per billion (ppb), respectively. Final gas purification was carried out by two crucibles filled with "Mischmetall" placed in front and behind the reaction vessel. Undoped samples were arc-welded into a niobium ampule under 800 mbar of argon which was purified by a titanium sponge at 600 °C, silica gel and molecular sieves. The niobium container was sealed in an evacuated silica tube and heated at 1000 °C for 8 hours. As-prepared samples were obtained as white to light grey (undoped) or greenish to yellowish (Pr^{3+}- and Eu^{2+}-doped) polycrystalline powders.

Due to the air- and moisture-sensitive nature of the precursors and the final product, all manipulations of the starting materials and the final products was carried out in a nitrogen filled glovebox from GS Glovebox Systemtechnik with H_2O levels well below 60 ppm.

2.2. Elemental analysis

Nitrogen and oxygen contents were determined using a TC-400C from Leco Corporation, equipped with TCWin Analysis software, version 4.35, and Helium (4.6, Westfalen AG) as purge gas. For every analysis 5–10 mg of the material were weighed, transferred into tin capsules and sealed. For a more homogeneous melting of the samples three scraps of highly pure nickel wire were added before sealing the capsules. Analysis was conducted at 850 A in high purity carbon crucibles and repeated three times. An error was estimated following standard procedure using Eq. (1):

$$S = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(X_i - \bar{X})^2},$$

(1)

with n being the number of measurements, X_i is the value of measurement i, and $\bar{X}$ is the mean value.

2.3. X-ray diffraction

Phase formation and purity was investigated by X-ray diffractometry (XRD) using a Rigaku MiniFlex II, working in Bragg-Brentano ($\Theta/2\Theta$) geometry. Diffraction data was collected within a 2Θ range from 5° to 80° with a step width of 0.02° and an integration time of 1 s using Ni-filtered Cu-K_α radiation. The samples were covered by a protective foil (Scotch, Magic Tape 810) during measurements to ensure a sufficient shielding from moisture and air. For the refinement of the cell parameters SiO_2 (Merck, p. a.) was added to the samples prior to measurements and peak positions were corrected according to the internal standard. As-corrected data was indexed and refined using the Stoe WinX^{Pow} program.

2.4. Optical spectroscopy

PL emission as well as excitation spectra were recorded on an Edinburgh Instruments FSL 920 spectrometer equipped with a 450 W Xe arc lamp, mirror optics for powder samples and a cooled (-20 °C) single-photon counting photomultiplier from Hamamatsu (R2658P). For PL decay kinetics a μF 920 H Xe flash lamp (100 W) from Edinburgh Instruments was used as excitation source. Temperature dependent PL measurements in the range from 78–500 K were carried out applying an Oxford Instruments cryostat MicrostatN2. The cooling agent was liquid nitrogen. Accuracy of the temperature measurement was set to ± 3 K and the stabilization time to 60 s. Thermoluminescence spectra were recorded employing the same set-up. The sample was cooled to 80 K and excited for several minutes. Then, the excitation source was switched off and the sample was heated with a defined heating rate up to 500 K while PL emission intensity at a certain wavelength was monitored.

The correction file for the emission spectra was obtained from a tungsten incandescent lamp certified by the National Physics Laboratory, UK. Diffuse reflection (DR) spectra were recorded on a spectrometer of the same model, equipped with a "spectralon"-coated integration sphere. $BaSO_4$ (99.998%, Sigma-Aldrich) was used as a reflection standard. Analysis and handling of data was carried out with the F900 program issued by Edinburgh Instruments.

3. Results and discussion

Quite recently, we reported on the superstructure formation in $SrBa_8[BN_2]_6$, which is a result of electron-precise formulation and the ordering of strontium vacancies.[26] All prepared samples in this study were analyzed by powder X-ray diffraction (XRD) and indexed in the previously reported space group $Fd\bar{3}m$. The diffraction patterns and the reference are depicted in Fig. 1 along with an analysis of the lattice constants of the various doping concentrations (Table 1). Powder samples were all of single phase and matched the reference. The dopants at the applied concentration levels did not lead to a significant change of the lattice parameters (Table 1).

Undoped $SrBa_8[BN_2]_6$ was prepared in a niobium container to ensure that no residual activator ions from the tube furnace walls polluted the sample. None the less, the material exhibited bright