

Journal of Alloys and Compounds 385 (2004) 1-11

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Synthesis, structure, and luminescence properties of Eu^{2+} and Ce^{3+} activated $BaYSi_4N_7$

Y.Q. Li, G. de With, H.T. Hintzen*

Laboratory of Solid State and Materials Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands

Received 19 December 2003; received in revised form 20 April 2004; accepted 20 April 2004

Abstract

BaYSi₄N₇ and its phosphors activated with Eu²⁺ and Ce³⁺ were synthesized by solid-state reaction at 1400–1650 °C under nitrogen mixed with hydrogen atmosphere. The crystal structure of BaYSi₄N₇ was solved by direct methods and refined by the Rietveld method from powder X-ray diffraction data. BaYSi₄N₇ crystallizes in the hexagonal space group P6₃mc (No.186), with a = 6.0550 (2) Å, c = 9.8567 (1) Å, V = 312.96 (2) Å³, and Z = 2, which is isotypic with BaYbSi₄N₇. The photoluminescence properties have been studied for the solid solutions of Ba_{1-x}Eu_xYSi₄N₇ (x = 0 - 0.4) and BaY_{1-x}Ce_xSi₄N₇ (x = 0 - 0.1) at room temperature. Eu²⁺-doped BaYSi₄N₇ gives a broad green emission band centered between 503 and 527 nm depending on the Eu²⁺ concentration. The Eu²⁺ emission band shows a red-shift formulation with increasing Eu²⁺ concentration mainly caused by the change of the crystal field strength and Stokes shift. Concentration quenching of Eu²⁺ emission is observed for x = 0.05 due to energy transfer between Eu²⁺ ions by electric dipole–dipole interactions with a critical interaction distance of about 20 Å. Ce³⁺-doped BaYSi₄N₇ exhibits a bright blue emission band with a maximum at about 417 nm, which is independent of Ce³⁺ concentration. This is ascribed to a lower solubility of Ce³⁺ ions in BaYSi₄N₇ lattice as shown by X-ray powder diffraction analysis. © 2004 Elsevier B.V. All rights reserved.

Keywords: BaYSi₄N₇; Synthesis; Powder X-ray diffraction; Rietveld refinement; Luminescence; Europium; Cerium

1. Introduction

It is of considerable interest to develop advanced luminescent materials with high brightness and high efficiency for applications in fluorescent lamps, light emitting diodes (LED) and various kinds of display devices. Up to date, most of them are dominated by oxides, sulfides, halides and phosphides doped with transition metal or rare-earth ions [1–4]. Recent work has shown that nitride or oxynitride compounds are promising host lattices for luminescent materials [5–8], the presence of a significant covalent character of nitrogen atoms in the lattice may bring about some peculiar optical properties with respect to the traditional host lattice [9,10]. Hence, it is necessary to explore some new nitride compounds and furthermore build-up the relationships between the chemical composition, crystal structure and the resulting optical properties. A series of quaternary compounds containing trivalent Yb formed with alkaline-earth ions and silicon nitride, MYbSi₄N₇ (M = Sr, Ba and divalent Eu) have already been reported [11–13]. All of them are isotypic in space group P6₃mc, with Z = 2. This structure is composed of a network of corner-sharing SiN₄ tetrahedra. M²⁺ (M = Sr, Ba, and Eu) and Yb³⁺ reside within the Si₆N₆-ring channels. Besides common two-fold coordinated nitrogen atom or N^[2] bridges, unusual four-fold coordinated N^[4] atoms are also present, with significantly longer bond lengths than those of the Si–N bonds of the N^[2] atoms [14].

Considering the comparable ionic radius (Y³⁺: 0.9 Å; Yb³⁺: 1.02 Å) and the similarity of some Y and Yb containing silicon oxynitride compounds, it is therefore interesting to explore the possibility of isostructural compounds with substitution of Y for Yb with the intention of design of promising host lattices for doping with luminescent ions. Recently, we have reported about ab initio calculation of the crystal structure and electronic structure of MYSi₄N₇ (M = Sr, Ba) [15]. To systematically study those luminescent materials, powder samples of Ba_{1-x}Eu_xYSi₄N₇ (0 $\le x \le 1$)

^{*} Corresponding author. Tel.: +31-40-2472770; fax: +31-40-2445619. *E-mail address:* h.t.hintzen@tue.nl (H.T. Hintzen).

and BaY_{1-x}Ce_xSi₄N₇ ($0 \le x \le 0.1$) were prepared by the conventional solid-state reaction approach. In this paper, we describe the synthesis, and give further details about the crystal structure of BaYSi₄N₇. Another goal of this work is to investigate the structure using Eu or Ce as a structural (spectroscopic) probe and emphasize the structure–luminescence properties relationships of the powder samples activated with Eu²⁺ or Ce³⁺ ions.

2. Experimental

Powder samples of BaYSi₄N₇ and solid solutions of several Ba_{1-x}Eu_xYSi₄N₇ ($0 \le x \le 1$) and BaY_{1-x}Ce_xSi₄N₇ $(0 \le x \le 0.1)$ compounds were prepared by solid-state reaction from stoichiometric quantities of high purity grade Si₃N₄ (Cerac S-1177, measured β content: ~91%, N content: 38.35%, 99.5%), and the metals Y (Csre, 99.9%), Ba (Aldrich, 99%, pieces), Ce (Alfa, 99%) and Eu (Csre, 99.9%, pieces). The large pieces of the Ba and Eu metals rendered a homogeneous mixing procedure impossible, therefore, Ba₃N₂ and EuN were pre-synthesized by nitriding the Ba and Eu metals under a flowing pure nitrogen atmosphere at 550 and 850 °C, respectively, and subsequently grinding them into fine powders. The mixtures of raw materials were thoroughly mixed and ground with an agate mortar and pestle. Subsequently, the well-mixed powders were placed in a molybdenum crucible covered with a lid and fired twice at 1400 and 1650 °C for 12-24 h under a flowing gas of 5% H₂-95% N₂ in horizontal tube furnaces with an intermediate grinding between the firing steps. All manipulations were carried out in a nitrogen filled dry glove box due to the great air sensitivity of most of the raw materials.

Powder X-ray diffraction (XRD) data were collected at room temperature on a Rigaku D/Max-yB diffractometer operating at 40 kV, 30 mA with Bragg-Brentano geometry (flat graphite monochromator, Scintillation counter) using Cu Ka radiation. The sample was mounted on a standard flat plate aluminum sample holder. For the lattice parameters determination of both undoped and doped samples, powder diffraction data were recorded in the 2θ range of $10-90^{\circ}$ with step scan mode (step size $0.01^{\circ} 2\theta$, counting time per step 6s) while 15 wt.% silicon powder was used as an internal standard. For indexing and crystal structure determination XRD data were recorded with step scan within a 2θ range of 10–120° with a step size of $0.01^{\circ} 2\theta$ and a counting time of 20 s per step on the finely ground samples. A 1° divergence and scatter slit together with a 0.3° receiving slit were employed for measurement.

The photoluminescence spectra were determined at room temperature on the powder samples by a Perkin-Elmer LS-50B luminescence spectrometer with Monk–Gillieson type monochromators and a 20 kW xenon discharge lamp as excitation source. The radiation was detected by a red sensitive photomultiplier R928. The spectra were obtained in the range of 200–900 nm with a scanning speed of

100 nm/min and the selected excitation and emission slit width of 2.5 nm. Excitation spectra were automatically corrected; however, all the emission spectra were corrected by taking into account the effect of the combined spectral response of the detector of R928 and the monochromator using the measured spectra of a calibrated W-lamp as the light source.

Diffused reflectance spectra were recorded in the range of 230–700 nm with BaSO₄ white powder and black felt as the references.

3. Results and discussion

3.1. Structure determination of undoped $BaYSi_4N_7$

The prepared samples as examined by X-ray powder diffraction appeared to be single phase. The accurate position and integrated intensities of the first 2θ Bragg peaks were obtained by profile fitting with the program XFIT [16] using a split Pearson VII function. The powder X-ray diffraction pattern of BaYSi₄N₇ was then indexed on the basis of a primitive hexagonal cell with unit cell parameters a = 6.0525 (3) Å, c = 9.8525 (7) Å, and V = 312.57 Å³ ($M_{20} = 225.5$, $F_{20} = 193.3(0.0038, 27)$) by the powder indexing program of DICVOL91 [17,18] in the CRYSFIRE suite [19]. This result was also confirmed with TREOR90 [20]. The final refined lattice parameters using Si powder as an internal standard are listed in Table 1. Two formula units per primitive unit cell can be deduced from the lattice parameters and the measured density (4.105 g cm⁻³).

The systematic absences (2h-hl: l = 2n; h-2hl: l = 2n and hhl: l = 2n) suggest that the possible space groups could be P31c, P31c, P63mc, P62c and P63/mmc.

The crystal structure elucidation of $BaYSi_4N_7$ was carried out by ab initio crystal determination with the program EXPO [21] using EXTRA [22] for extraction of the integrated intensities by the Le Bail method [23] and SIRPOW97 [24] optimized for solving crystal structure by powder data

Table 1 Crystallographic data for BaYSi4N7

Formula	BaYSi ₄ N ₇
Formula weight	436.64
Crystal system	Hexagonal
Space group	P6 ₃ mc (no. 186)
Unit cell dimensions (Å)	a = 6.0550 (2)
	c = 9.8567 (1)
Cell volume (Å ³)	312.96 (2)
Ζ	2
Density, calculated (g/cm ³)	4.634
<i>T</i> (K)	298
2θ (degree) range	10-120
Scan conditions	Step size: 0.01, 20 s/step
<i>R</i> -factors	
$R_{ m wp}$	0.0860
R _p	0.0538

Table 2 Atomic coordinates and isotropic displacement parameters of $BaYSi_4N_7~({\rm \AA}^2)$

Atom	Wyckoff position	Symmetry	x	у	Z	U
Ba	2b	C _{3v}	1/3	2/3	0.3627(3)	0.0035 (3)
Y	2b	C _{3v}	1/3	2/3	0.7372 (3)	0.0016 (4)
Si1	2a	C_{3v}	0	0	0.3136 (4)	0.0022 (9)
Si2	6 <i>c</i>	Cs	0.1732 (2)	0.3464 (3)	0.0465 (3)	0.0036 (4)
N1	6 <i>c</i>	C _s	0.0276 (10)	0.5138 (5)	0.0996 (4)	0.0020 (13)
N2	6 <i>c</i>	Cs	0.8461 (3)	0.6921 (7)	0.3730 (5)	0.0022 (11)
N3	2a	C_{3v}	0	0	0.1230 (8)	0.0096 (19)

for direct methods. All the possible space groups were used as input to the EXPO program to derive the atomic position with direct methods in the range of $10-70^{\circ} 2\theta$ because of the strong intensity decrease at large 2θ range.

With photoluminescence spectroscopy (see photoluminescence section) on Eu²⁺- and Ce³⁺-doped BaYSi₄N₇ (Eu and Ce probes are assumed to partially replace Ba and Y atom in the lattice) only one relatively high symmetric emission band can be observed for each of them. It is clearly suggested that there is only one Ba and Y site in the BaYSi₄N₇ primitive lattice and those sites should have high point symmetry. From the primary results of EXPO program, the most probable point symmetry group for both Ba and Y ions might be C_{3v} with the highest site symmetry, consistent with the space group of P6₃mc and P6₃/mmc mentioned above. Combining this information together with the output results of the EXPO program, the position of all Ba, Y, Si and N atoms in the unit cell was obtained. The results using the space group $P6_3mc$ gave a lower structural R factor as compared with that of the P63/mmc. Consequently, in the further structure refinement stage, only the space group P63mc was applied to carry out the Rietveld refinement. All of the above results are similar to those obtained from a single crystal study of BaYbSi₄N₇ [10–13].

The structure of BaYSi₄N₇ was refined by the Rietveld method [25] using the initial coordination of atoms obtained from the above mentioned direct methods based on the space group P6₃mc. Rietveld refinement was performed using the program GSAS [26,27] in the range $10-120^{\circ} 2\theta$. The scaling factor, the zero point, the background and the lattice parameters were refined initially. The profile fitting was used a pseudo-Voigt function corrected for asymmetry. The preferential orientation was also refined using the March-Dollase function because of the needle-like morphology of BaYSi₄N₇ particle. All atom positions and thermal displacement factors were refined and the final refinement converged to the residual factors $R_{wp} = 8.60\%$ and $R_{\rm p} = 5.38\%$. Fig. 1 shows the final simulation of the calculated and observed diffraction patterns. The crystallographic data are listed in Table 1 and the atomic coordinates are given in Table 2, and some selected bond distances and angles are summarized in Table 3.

BaYSi₄N₇ is isostructural with BaYbSi₄N₇ and also contains a three-dimensional network structure of corner-sharing SiN₄ tetrahedra ${}^3_{\infty}[(Si_3^{[4]}N_6^{[2]}N^{[4]})^{5-}]$. In this network, the N^[4] atoms connect four Si atoms and the N^[2] atoms connect two Si atoms without the presence of N^[3] atoms as generally observed in metal-silicon nitrides. The structure can be considered as an infinite building of tetrahedral units of $[N(SiN_3)_4]$ joined by sharing $N^{[2]}$ atoms along the *b*-axis (Fig. 2a). Both Ba^{2+} and Y^{3+} ions occupy one site in the primitive lattice and are located in channels along [100] formed by Si₆N₆ rings, as shown in Fig. 2. The Ba atom is surrounded by 12 nearest nitrogen neighbours: six N2 with long-distances are in the same planar hexagonal array ((Ba1)(N2)₆ layer), and six N1 with short-distances (three above and three below the $(Ba1)(N2)_6$ layer) form a hexagonal anti-prism (or a distorted octahedron) around the central atom of Ba in the cubic closest packing (CCP) framework composed of the stacking of four $(Ba^{2+})(N^{3-})_n$ layers. The Y atom is six-fold coordinated by N ($3 \times N1$, $3 \times N2$) forming a slight distorted octahedron. The local coordination environments of Ba and Y by N atoms are presented in Fig. 2b and c. As compared with BaYbSi₄N₇, the main structural difference is that the bond lengths of most of Ba-N and Y-N as well as Si-N in BaYSi₄N₇ become longer since the ionic radius of Y^{3+} is larger than that of Yb^{3+} ion (see Table 3) which results in the unit cell volume increase. The Ba-N bond lengths



Fig. 1. Observed (crossed) and calculated (line) X-ray powder diffraction pattern as well as difference profile (bottom line) between observed and calculated intensity of the Rietveld refinement of BaYSi₄N₇. Positions of Bragg reflections are marked by vertical short lines.

Table 3

Selected interatomic distances (Å) and angles (degree) for BaYSi₄N₇

Ba–N1	3.048 (6)
Ba-N1 ^{vii}	3.006 (6)
Ba-N1 ^{viii}	3.049 (6)
Ba–N1 ^{ix}	3.006 (6)
Ba–N1 ^{xi}	3.048 (6)
Ba–N1 ^{xii}	3.006 (6)
Ba–N2 ^{xiv}	3 03167 (28)
Ba-N2	3.03262 (28)
Ba-N2 ^{xv}	3.03202(28)
Ba-N2 ^{viii}	3.03221(28)
$B_{2}-N2^{xi}$	3.03234(28)
$B_{2}-N2^{xvi}$	3.03234(28)
Da-112	5.05177 (20)
Y–N1 ^{vii}	2.328 (5)
Y–N1 ^{ix}	2.328 (5)
Y–N1 ^{xii}	2.329 (5)
Y-N2 ^{vi}	2.309 (5)
Y-N2 ^x	2.309 (5)
Y-N2 ^{xiii}	2.309 (5)
D V	2 (010 (0)
Ba-Y	3.6919 (9)
Ba-Y	3.70825 (33)
Ba-Y ⁿ	3.70825 (33)
Ba-Y ⁱⁱⁱ	3.70775 (33)
N1-Ba-N1 ^{vii}	145,740 (34)
N1–Ba–N1 ^{viii}	54 19 (16)
N1–Ba–N1 ^{ix}	109 256 (14)
N1_Ba_N1 ^{xi}	54 19 (16)
N1_Ba_N1 ^{xii}	$145\ 720\ (34)$
N1 Ba N2 ^{xiv}	65 51 (13)
N1 B ₂ N2	110.67(14)
N1 Do N2XV	119.07(14)
N1-Da-N2 N1VII Do N1VIII	90.32(10)
NI - Da - NI	143.725(34)
N1 ^{VI} – Ba–N1 ^{VI}	100.08(15)
	109.256 (14)
N1 ^{vii} – Ba–N1 ^{vii}	00.08 (15) 86.02 (10)
	86.92 (10)
N1 ^m -Ba-N2	86.91 (10)
N1 ^m –Ba–N2 ^m	122.13 (14)
NI ^{vin} –Ba–NI ^{ix}	145.723 (34)
N1 ^{viii} –Ba–N1 ^{xi}	54.19 (16)
N1 ^{vm} –Ba–N1 ^{xn}	109.240 (14)
N1 ^{viii} –Ba–N2 ^{xiv}	119.68 (14)
N1 ^{vin} –Ba–N2	65.50 (13)
N1 ^{vin} –Ba–N2 ^{xv}	145.740 (34)
N1 ^{1x} –Ba–N1 ^{x1}	66.08 (15)
$N1^{1x}$ -Ba- $N1^{x11}$	56.17 (12)
N1 ^{ix} -Ba-N2 ^{xiv}	122.13 (14)
N1 ^{ix} –Ba–N2	86.91 (10)
N1 ^{xi} –Ba–N1 ^{xii}	145.720 (34)
N1 ^{xi} –Ba–N2 ^{xiv}	90.33 (10)
N1 ^{xi} –Ba–N2	90.32 (10)
N1 ^{xi} –Ba–N2 ^{xv}	119.67 (14)
N1 ^{xii} –Ba–N2 ^{xiv}	122.14 (14)
N1 ^{xii} –Ba–N2	56.16 (12)
N1 ^{xii} –Ba–N2 ^{xv}	56.16 (12)
N2 ^{xiv} –Ba–N2	173.66 (17)
N2 ^{xiv} –Ba–N2 ^{xv}	119.888 (13)
N2–Ba–N2 ^{xv}	64.99 (13)
Staviji st Staje	00.40.50
$N1^{vir} - Y - N1^{ix}$	89.49 (20)
$N1^{vn} - Y - N1^{xn}$	89.48 (20)
$N1^{vn}$ -Y-N2 ^{vn}	90.39 (13)
N1 ^{vn} -Y-N2 ^x	179.8123 (7)
$N1^{vn}$ -Y- $N2^{xnn}$	90.38 (13)

Table 3	(Continued)	
---------	-------------	--

N1 ^{ix} -Y-N1 ^{xii}	89.48 (20)
N1 ^{ix} -Y-N2 ^{vi}	90.39 (13)
N1 ^{ix} -Y-N2 ^x	90.38 (13)
N1 ^{ix} -Y-N2 ^{xiii}	179.8062 (7)
N1 ^{xii} –Y–N2 ^{vi}	179.8219 (6)
N1 ^{xii} –Y–N2 ^x	90.37 (13)
N1 ^{xii} –Y–N2 ^{xiii}	90.37 (13)
N2 ^{vi} -Y-N2 ^x	89.76 (19)
N2 ^{vi} -Y-N2 ^{xiii}	89.76 (19)
N2 ^x -Y-N2 ^{xiii}	89.75 (19)

Symmetry codes: (i) x - y, x, -0.5 + z; (ii) 1 + x - y, x, -0.5 + z; (iii) 1 + x - y, 1 + x, -0.5 + z; (iv) x, 1 + y, z; (v) 1 + x, 1 + y, z; (vi) x - y, x, 0.5 + z; (vii) 1 + x - y, 1 + x, 0.5 + z; (viii) 1 - y, 1 + x - y, z; (ix) -x, 1 - y, 0.5 + z; (x) 1 - x, 1 - y, 0.5 + z; (xi) -x + y, 1 - x, z; (xii) y, -x + y, 0.5 + z; (xiii) y, 1 - x + y, 0.5 + z; (xiv) -1 + x, y, z; (xv) 1 - y, x - y, z; (xvi) 1 - x + y, 0.5 + z; (xvii) 1 + x - y, 1 + z; (xvii) 1 + x - y, 1 + z; (xviii) -x + y, 1 - x, 1 + z; (xviii) -1 + x, -1 + y, z; (xviii) x, -1 + y, z; (xviii) -x, -y, 0.5 + z; (xviv) x, y, -1 + z; (xvv) 1 - x, 1 - y, -0.5 + z; (xvvii) 1 + x, y, z; (xvvii) -y, x - y, z; (xvviii) -x, y, -x, z.

vary from 3.006 to 3.049 Å and the Y–N bond lengths vary from 2.309 to 2.329 Å (three long and three short bonds).

3.2. Solubility of Eu and Ce ions in the BaYSi₄ N_7 host lattice

The position of the emission band and efficiencies can be tuned by varying the Eu or Ce concentration due to altering the lattice parameters of the BaYSi₄N₇ host which results in changing crystal field strength and covalency. Therefore, it is of interest to know the solubility limit of Eu or Ce ions in the BaYSi₄N₇ lattice. Considering the cation radius [28] and the valence states, we supposed that Eu²⁺ ions prefer to occupy Ba sites, while Ce³⁺ ions prefer to occupy Y sites. Accordingly, series of doped Eu and Ce samples were investigated, respectively.

Fig. 3 shows the lattice parameters as function of the concentration for $Ba_{1-x}Eu_xYSi_4N_7$ (0 < x < 1) (Fig. 3a) and $BaY_{1-x}Ce_xSi_4N_7$ (0 $\leq x < 0.1$) (Fig. 3b). For $Ba_{1-x}Eu_xYSi_4N_7$, the lattice parameters a, c and the unit cell volume V, nearly linearly decrease with the Eu^{2+} concentration in the whole range because of the substitution of small Eu^{2+} for the large Ba^{2+} in ionic radius [28], while above x = 0.4, a secondary phase YSi₃N₅ can be observed. Although $Ba_{1-x}Eu_xYSi_4N_7$ can form the complete solid solutions between BaYSi₄N₇ and EuYSi₄S₇, the largely different interatomic distances in their framework hinder $Ba_{1-x}Eu_xYSi_4N_7$ existing in a purity phase. On the other hand, the lattice parameters for $BaY_{1-x}Ce_xSi_4N_7$ exhibit only a slight tendency to increase with an increase of x due to the ionic radius of Ce³⁺ being significantly larger than that of Y^{3+} . It also can be seen from Fig. 3b that variation in Ce concentration does change much less the lattice parameters. Due to this limited solubility an unknown secondary phase is present in Ce-doped BaYSi₄N₇ for x > 0.05.



Fig. 2. Schematic views of the crystal structure of $BaYSi_4N_7$. (a) Projection of tetrahedral representation of the crystal structure of $BaYSi_4N_7$ along [100] direction. The Ba^{2+} ions are shown as large grey spheres and the Y^{3+} ions as small black spheres. (b) Coordination of the Ba atoms and (c) coordination of the Y atoms in $BaYSi_4N_7$ with nitrogen atoms.

In order to differentiate the interatomic distances and angles between undoped and Eu^{2+} and Ce^{3+} doped BaYSi₄N₇, the Rietveld refinement was performed using powder XRD data with the structural model based on the results for BaYSi₄N₇. The observed and difference Rietveld plots are given in Fig. 4. The summary of crystallographic data, including the atomic coordination for Eu^{2+} and Ce^{3+} doped BaYSi₄N₇, are given in Table 4 and selected distances and bond angles given in Table 5. The Eu–N2 bond becomes shorter, whereas the distances of the Eu–N1 bonds are similar with the Ba–N1 distances in undoped BaYSi₄N₇ lattice. On the other hand the average Y/Ce–N distances are not significantly changed in comparison with Y–N distances of the undoped sample (as shown in Tables 3–5). The site-occupancy factors (Table 4), reveal that the Y³⁺ sites reject Ce³⁺ ions surpassing 1 mol% to occupy its 2*b* sites in the BaYSi₄N₇ lattice, which confirms that only a small amount of Ce³⁺ ions can be incorporated into BaYSi₄N₇.



Fig. 3. The concentration of Eu and Ce dependence of the lattice parameters of (a) $Ba_{1-x}Eu_xYSi_4N_7$ ($0 \le x \le 1$) and (b) $BaY_{1-x}Ce_xSi_4N_7$ ($0 \le x < 0.1$).

3.3. Diffuse reflection of Eu and Ce doped $BaYSi_4N_7$

The daylight colour of undoped, Eu, and Ce-doped samples are gray–white, green–yellow and antique-white, respectively. The typical diffuse reflectance spectra for undoped BaYSi₄N₇, Ba_{0.9}Eu_{0.1}YSi₄N₇ and BaY_{0.97}Ce_{0.03}Si₄N₇ are shown in Fig. 5. The spectrum of Eu-doped BaYSi₄N₇ is described by one broad absorption feature centered between 310 and 350 nm depending on the concentration of the Eu ions. Because the undoped sample does not present such absorption, it is implied that the absorption originates from Eu²⁺. Addition of Eu²⁺ to form Ba_{1-x}Eu_xYSi₄N₇ solid solution has a significant influence on the onset of absorption. The onset of the absorption band of Eu ions systemically shifts to longer wavelength up to x = 0.3 (see inset in Fig. 5a) corresponding to the solubility limit of Eu ions in the BaYSi₄N₇ host (Fig. 3a).

In contrast, except for the absorption intensity enhancement with the Ce concentration increasing no significant effects on the onset of absorption for all $BaY_{1-x}Ce_xSi_4N_7$ samples (x = 0-0.1) could be observed. Clearly, the absorption below 260 nm is attributed to the valence to conduction band transitions of the host lattice. This is in agreement with our calculated predictions as reported earlier [15]. In addition, the absorption band of $BaY_{1-x}Ce_xSi_4N_7$ shows two distinctly separated sub-bands (313 and 334 nm, see inset in Fig. 5b), which is ascribed to splitting of the 4f \rightarrow 5d excitation band of the Ce³⁺ ion.

3.4. Luminescence of BaYSi₄N₇:Eu

Fig. 6 shows the room-temperature emission spectra of $Ba_{1-x}Eu_xYSi_4N_7$ ($0 < x \le 0.4$). The inset displays the corresponding excitation spectra from bottom to top. Since we

Table 4 Crystal data and refined atomic coordinations for Ba_{0.9}Eu_{0.1}YSi₄N₇ and BaY_{0.97}Ce_{0.03}Si₄N₇

Formula	$Ba_{0.9}Eu_{0.1}YSi_4N_7$	$BaY_{0.97}Ce_{0.03}Si_4N_7$				
Formula weight	Havagenal	Havagenel				
Space group	$P_{6}m_{c}$ (no. 186)	P_{6} mc (no. 186)				
Space group	1 03me (no. 180)	1 03mc (no. 180)				
Unit cell dimensions						
a (Å)	6.0520 (4)	6.0550 (1)				
<i>c</i> (Å)	9.8540 (1)	9.8563 (1)				
Cell volume V (Å ³)	312.56 (3)	312.90 (2)				
Z	2	2				
Density, calculated						
T (K)	298	298				
2θ (deg.) range	10-120	10-120				
Scan conditions	step size: 0.01, 20 s/step	step size: 0.01, 20 s/step				
R-factors						
R _{wp}	0.0979	0.0896				
$R_{\rm p}$	0.0643	0.0560				
Atom	Wyckoff position	x	у	z	U	g^*
$Ba_{0.9}Eu_{0.1}YSi_4N_7$						
Ba	2b	1/3	2/3	0.3625 (1)	0.0052 (4)	0.90 (6)
Eu	2b	1/3	2/3	0.3625 (1)	0.0052 (4)	0.10 (6)
Y	2b	1/3	2/3	0.7370 (1)	0.0023 (6)	1.0
Si1	2a	0	0	0.3127 (6)	0.0019 (11)	1.0
Si2	6 <i>c</i>	0.1729 (2)	0.3458 (4)	0.0458 (4)	0.0047 (6)	1.0
N1	6 <i>c</i>	0.0290 (12)	0.5145 (6)	0.0985 (7)	0.0048 (17)	1.0
N2	6 <i>c</i>	0.8477 (4)	0.6952 (8)	0.3708 (7)	0.0035 (14)	1.0
N3	2a	0	0	0.1195 (13)	0.0085 (22)	1.0
BaY _{0.97} Ce _{0.03} Si ₄ N ₇						
Ва	2b	1/3	2/3	0.3625 (1)	0.0045 (4)	1.0
Y	2b	1/3	2/3	0.7373 (1)	0.0030 (6)	0.993 (8)
Ce	2b	1/3	2/3	0.7373 (1)	0.0030 (6)	0.007 (8)
Si1	2a	0	0	0.3144 (5)	0.0026 (9)	1.0
Si2	6 <i>c</i>	0.1730 (2)	0.3460 (3)	0.0464 (3)	0.0052 (5)	1.0
N1	6 <i>c</i>	0.0265 (10)	0.5133 (5)	0.0989 (6)	0.0011 (13)	1.0
N2	6 <i>c</i>	0.8478 (4)	0.6955 (8)	0.3700 (6)	0.0031 (12)	1.0
N3	2a	0	0	0.1248 (10)	0.0076 (20)	1.0

Constraint on occupancy (g^*) : g(Ba) + g(Eu) = 1.0 for $Ba_{0.9}Eu_{0.1}YSi_4N_7$; g(Y) + g(Ce) = 1.0 for $BaY_{0.97}Ce_{0.03}Si_4N_7$.

could not obtain single-phase EuYSi₄N₇ and Eu-rich solid solution samples ($0.5 \le x < 1$), the luminescence properties in this range will not be described in this paper.

The excitation spectra for $Ba_{1-x}Eu_x YSi_4N_7$ (0 < x \leq 0.4) exhibit two remarkable broad excitation bands with maxima around 342 and 386 nm together with a weak band near 283 nm (Fig. 6). The latter band is ascribed to host-lattice excitation (Fig. 5a), in agreement with the fact that its position is independent of the Eu concentration in contrast to the other bands (Table 6). As the Eu^{2+} concentration increases the long-wavelength excitation band shifts from about 383 to 388 nm, while the short-wavelength excitation band shifts from about 348 to 346 nm (Table 6). This is a consequence of a larger crystal field splitting (CFS) due to shrinkage of the lattice when the Ba^{2+} ion is replaced by the smaller Eu^{2+} ion. As compared with Eu-doped Ba₂Si₅N₈, the excitation bands above 400 nm [8,9] are absent in BaYSi₄N₇:Eu, which is related to a different crystal and electronic structure as well as number of cross-linking SiN₄ tetrahedra ($N^{[x]}$).

The emission spectra of $Ba_{1-x}Eu_xYSi_4N_7$ ($0 < x \le 0.4$) consist of a single broad band with a nearly symmetric profile in the green spectral region. It is well known that Eu^{2+} ions show emission bands, while Eu^{3+} displays sharp emission lines due to $4f \rightarrow 4f$ transitions of 5D_0 to 7F_J (J = 0-6) around 580–630 nm [1]. As no $4f \rightarrow 4f$ emission lines originating from Eu^{3+} in the red spectral area can be observed, the broad green emission band can be assigned to the $4f^65d$ $\rightarrow 4f^7$ transition of Eu^{2+} , indicating that the Eu ions in the nitride or oxynitride compounds are reduced to Eu^{2+} [9].

The position of the broad emission band shifts to longer wavelengths (Fig. 6) with an increase of Eu^{2+} concentration (from 503 to 527 nm), as expected for Eu^{2+} in a shrinking lattice. Due to the associated smaller interatomic distances, the crystal field strength around Eu^{2+} increases (Table 6), which results in increasing splitting of the 5d levels and lowering of the level from which emission occurs. In addition, a larger Stokes shift is induced (Table 6), because a stronger relaxation is promoted for Eu^{2+} on a site becoming smaller.



Fig. 4. Observed (crossed), calculated (line) X-ray powder diffraction pattern and the difference profile (bottom line) between observed and calculated intensity of the Rietveld refinement of (a) $Ba_{0.9}Eu_{0.1}YSi_4N_7$, and (b) $BaY_{0.97}Ce_{0.03}Si_4N_7$ samples. The vertical markers show the positions calculated for Bragg reflections.

Consequently the red-shift of the emission band for higher Eu contents can be understood.

The interaction between the host lattice and the activator Eu^{2+} becomes stronger with increasing Eu^{2+} concentration which results in broadening of the emission band (Fig. 7). Such behavior is ascribed to the strong coupling of the electronic states of the Eu^{2+} center with vibrational modes of the host lattice [29]. The width of the emission band is also related to the Stokes shift, generally, a broad emission band corresponds to a large Stokes shift [1]. This relation is in satisfactory agreement with the results observed for $Ba_{1-x}Eu_xYSi_4N_7$ (0 < $x \le 0.4$) phosphors (Fig. 7, Table 6).

Concentration quenching of the luminescence becomes effective for Eu^{2+} contents surpassing 5 mol% because the distance between Eu^{2+} ions becomes smaller due to the replacement of Ba with Eu ions, which leads to the energy transfer between Eu^{2+} centers. The critical distance for the energy transfer between identical Eu^{2+} centers in BaYSi₄N₇ can be estimated by the formula (1) [30]



Fig. 5. Typical diffuse reflectance spectra of $BaYSi_4N_7$, $Ba_{0.9}Eu_{0.1}YSi_4N_7$ and $BaY_{0.97}Ce_{0.03}Si_4N_7$. The inset in (a) is the onset of absorption dependence of the Eu^{2+} concentration. The inset in (b) shows the magnified part of the reflection pattern around Ce^{3+} absorption band.

$$R_{\rm c} \approx 2 \left(\frac{3V}{4\pi X_{\rm c} N}\right)^{1/3} \tag{1}$$

where X_c is the critical concentration, N is the number of Ba²⁺ ions in the unit cell, and V is the volume of the unit

Table 5 Selected interatomic distances (Å) for $Ba_{0.9}Eu_{0.1}YSi_4N_7$ and $BaY_{0.97}Ce_{0.03}Si_4N_7$

Ba _{0.9} Eu _{0.1} YSi ₄ N ₇		BaY _{0.97} Ce _{0.03} Si ₄ N ₇		
Bond	Length (Å)	Bond	Length (Å)	
Eu–N1	3.051 (7)	Ba–N1	3.055 (6)	
Eu-N1	3.003 (7)	Ba–N1	2.999 (6)	
Eu-N1	3.051 (7)	Ba–N1	3.055 (6)	
Eu-N1	3.003 (7)	Ba–N1	2.999 (6)	
Eu-N1	3.051 (7)	Ba–N1	3.055 (6)	
Eu-N1	3.003 (7)	Ba–N1	2.999 (6)	
Eu-N2	3.03017 (35)	Ba–N2	3.03176 (29)	
Eu-N2	3.03138 (35)	Ba–N2	3.03212 (29)	
Eu-N2	3.03078 (35)	Ba–N2	3.03176 (29)	
Eu-N2	3.03078 (35)	Ba–N2	3.03211 (29)	
Eu-N2	3.03110 (35)	Ba–N2	3.03212 (29)	
Eu-N2	3.03050 (35)	Ba–N2	3.03176 (29)	
Y-N1	2.338 (7)	Ce-N1	2.328 (5)	
Y-N1	2.338 (7)	Ce-N1	2.328 (5)	
Y-N1	2.339 (7)	Ce-N1	2.328 (5)	
Y-N2	2.309 (6)	Ce-N2	2.306 (5)	
Y-N2	2.310 (6)	Ce–N2	2.306 (5)	
Y-N2	2.310 (6)	Ce–N2	2.306 (5)	



Fig. 6. The emission spectra of BaYSi₄N₇:Eu with varying Eu concentration (385 nm excitation wavelength at room temperature). In the inset, the corresponding excitation spectra are shown from bottom to top (monitoring at 510 nm emission wavelength).



Fig. 7. The Eu²⁺ concentration dependence of the emission intensity and width (FWHM) of the emission bands of $Ba_{1-x}Eu_xYSi_4N_7$ (0 < $x \le 0.4$).

cell. The estimated value for the energy transfer distance $R_{\rm c}$ between Eu²⁺ ions in BaYSi₄N₇ is approximately 20 Å, which is similar to the R_c value for Eu²⁺ centers in several oxide and apatite lattices [31,32].

Table 6 Spectral parameters of the $Ba_{1-x}Eu_xYSi_4N_7$ (x = 0-0.4) and $BaY_{1-x}Ce_xSi_4N_7$ (x = 0-0.5)



Fig. 8. Observed relative intensity of Eu²⁺ emission dependence of the concentration of $Ba_{1-x}Eu_xYSi_4N_7$ (0 < x \leq 0.4) under 385 nm excitation wavelength.

Energy transfer is generally associated with multipolar interactions, radiation reabsorption or exchange [33]. Based on the calculated R_c value and the broad emission band with high symmetry and small spectral overlap with the excitation band, it seems that multipolar interactions are the most relevant to Eu^{2+} energy transfer [1,30,33]. The type of multipolar interactions between the Eu^{2+} ions can be identified by examining the concentration dependence of the emission intensity from the emitting level which has multipolar interaction [34,35]. The emission intensity per activator ion can be expressed by the equation for weakly absorbed exciting radiation:

$$\frac{I_{\rm obs}}{x} = (1 + \beta'(x)^{\theta/3})^{-1}$$
(2)

where x is the activator concentration; I_{obs} is the observed relative emission intensity; β' is a constant for each interaction for a given host crystal and $\theta = 6, 8, 10$ for dipole-dipole, dipole-quadrupole, quadrupole-quadrupole interaction, respectively.

The I_{obs}/x versus x curve of the $4f^65d \rightarrow 4f^7$ emission from $Ba_{1-x}Eu_xYSi_4N_7$ (0 < $x \le 0.4$) is shown in Fig. 8.

Sample	Excitation maximum (nm)	Emission maximum (nm)	Stokes shift (cm ⁻¹)	$CFS (cm^{-1})$
$\overline{\text{Ba}_{1-x}\text{Eu}_x\text{YSi}_4\text{N}}$	I ₇			
0.02	283, 348, 383	503	6200	2600
0.10	283, 349, 385	508	6300	2700
0.20	283, 349, 388	517	6400	2900
0.30	283, 348, 389	526	6800	3000
0.40	283, 346, 388	537	7200	3100
BaY _{1-x} Ce _x Si ₄ N	I ₇			
0.01	285, 297, 317, 339	416	5500	4100
0.03	285, 297, 318, 338	417	5600	4100
0.05	285, 297, 319, 338	419	5700	4100



Fig. 9. The excitation ($\lambda_{em} = 420 \text{ nm}$) and emission spectra ($\lambda_{exc} = 338 \text{ nm}$) of BaY_{1-x}Ce_xSi₄N₇ (0 < x < 0.1) varied with the Ce³⁺ concentration. The dash curves in the inset figure for the emission spectrum x = 0.01 represent deconvoluted Gaussians.

The I_{obs}/x data of the emission over the Eu²⁺ concentration range of 0.1–0.4 mole fraction, can be fitted with a straight line with a slope of about –1.94. This corresponds to θ = 5.8, which indicates that electric dipole–dipole interaction is responsible for the concentration quenching of Eu²⁺ emission.

3.5. Luminescence of BaYSi₄N₇:Ce

The excitation spectra of BaYSi₄N₇:Ce³⁺ exhibit four bands at 338, 318, 297 and 285 nm (Fig. 9). Similar to BaYSi₄N₇:Eu²⁺ the band at about 285 nm is ascribed to host–lattice excitation, and the remaining peaks to splitting of the 5d band into 3 levels as expected for the incorporation of Ce³⁺ on the slightly distorted octahedral YN₆ site in BaYSi₄N₇ with point symmetry C_{3v}.

A relatively narrow emission band centered at about 417 nm can be distinguished in the emission spectra, in agreement with the substitution of Ce^{3+} ions on a single site. A decomposition of the emission band into two Gaussian-shaped bands is displayed in an inset in Fig. 9. The energy gap between the fitted two maxima is about 2009 cm^{-1} , which is in agreement with the value of the spin–orbit splitting of Ce^{3+} ground state of 4f configuration. Therefore, the emission of the Ce^{3+} in BaYSi₄N₇ can be assigned to the transition of 5d \rightarrow 4f (${}^2F_{5/2}$, ${}^2F_{7/2}$).

As can be seen from Fig. 9, no significant shifts of both Ce^{3+} excitation and emission bands are observed upon increasing the Ce^{3+} concentration. The lowest excitation band is located at 338 nm, thus resulting for all Ce concentrations in about the same Stokes shift (\approx 5600 cm⁻¹, Table 6) as well as CFS data (Table 6). An untunable Ce³⁺ emission band by

varying the Ce^{3+} concentration is related to the limited solubility of Ce^{3+} ions in $BaYSi_4N_7$ lattice. As a consequence, the effect of Ce^{3+} substitution for Y^{3+} ions is very slight.

4. Conclusions

A new compound, BaYSi₄N₇, has been synthesized by solid-state reactions and the crystal structure was determined from X-ray powder diffraction data with direct methods. BaYSi₄N₇ exhibits strong structural similarities to the already known BaYbSi₄N₇. The compound crystallizes in the hexagonal crystal system, space group P6₃mc, Z = 2, unit cell parameters a = 6.0550 (2) Å, c = 9.8567 (1) Å, and V = 312.96 (2) Å³. The refinement was carried out using the Rietveld method and the residual factors of the final refinement are $R_{wp} = 0.0860$, $R_p = 0.0538$. The structure of BaYSi₄N₇ contains one crystallographically distinct site for Ba and Y atoms, respectively. The Ba atoms are twelvefold coordinated by nearest nitrogen neighbours and the Y atoms are located inside a slightly distorted octahedron consisting of nitrogen atoms.

The optical properties of the $Ba_{1-x}Eu_xYSi_4N_7$ (x = 0-0.4) and $BaY_{1-x}Ce_xSi_4N_7$ (x = 0-0.1) have been studied using diffuse reflectance, UV excitation and emission spectroscopy. The interatomic distances for the local coordination of Eu and Ce atoms in Eu²⁺- and Ce³⁺-doped samples were also obtained by the Rietveld analysis. One broad Eu²⁺ green emission band with a maximum intensity around 503–527 nm emission center was observed depending on the Eu²⁺ concentration which can be assigned to the transition 4f⁶5d¹ \rightarrow 4f⁷. Varying the Eu²⁺ concentration results in a significant red-shift and broadening of the Eu²⁺ emission as well as a decrease of the emission intensity. The changes in the emission spectra have been associated with changes in the crystal field strength, Stokes shift and possibly the covalency around Eu²⁺ ions, as concluded from the variation of lattice parameters with Eu concentration and the Rietveld refinement data. As possible concentration is proposed for Eu²⁺ emission. In BaY_{1-x}Ce_xSi₄N₇ (x = 0-0.1), a rather narrow Ce³⁺ emission band around 417 nm is observed, its position almost independent of Ce³⁺ concentration.

References

- G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer-Verlag, Berlin, 1994.
- [2] K.H. Butler, Fluorescent Lamp Phosphors, The Pennsylvania State University Press, University Park, PA, 1980.
- [3] T. Justel, H. Nikol, C. Ronda, Angew. Chem. Int. Ed. Engl. 37 (1998) 3084.
- [4] C. Feldmann, T. Justel, C.R. Ronda, P.J. Schmidt, Adv. Funct. Mater. 13 (2003) 511.
- [5] J.W.H. van Krevel, H.T. Hintzen, R. Metselaar, A. Meijerink, J. Alloys Compd. 268 (1998) 272.
- [6] J.W.H. van Krevel, J.W.T. van Rutten, H. Mandal, H.T. Hintzen, R. Metselaar, J. Solid State Chem. 165 (2002) 19.
- [7] K. Uheda, H. Takizawa, T. Endo, J. Lumin. 87-89 (2000) 967.
- [8] H.A. Hoppe, H. Lutz, P. Morys, W. Schnick, A. Seilmeier, J. Phys. Chem. Solids 61 (2000) 2001.
- [9] J.W.H. van Krevel, Ph.D. thesis, Eindhoven University of Technology, 2000.
- [10] R. Marchand, F. Tessier, A. Le Sauze, N. Diot, Int. J. Inorg. Mater. 3 (2001) 1143.

- [11] H. Huppertz, W. Schnick, Angew. Chem. Int. Ed. Engl. 108 (1996) 2115.
- [12] H. Huppertz, W. Schnick, Z. Anorg. Allg. Chem. 212 (1997) 623.
- [13] H. Huppertz, W. Schnick, Acta Cryst. C53 (1997) 1751.
- [14] W. Schnick, H. Huppertz, Chem. Eur. J. 3 (1997) 679.
- [15] C.M. Fang, Y.Q. Li, H.T. Hintzen, G. de With, J. Mater. Chem. 13 (2003) 1480.
- [16] R.W. Cheary, A.A. Coelho, J. Appl. Cryst. 25 (1992) 109.
- [17] D. Louer, M. Louer, J. Appl. Cryst. 5 (1972) 271.
- [18] A. Boultif, D. Louer, J. Appl. Cryst. 24 (1991) 987.
- [19] R. Shirley, The Crysfire 2002 System for Automatic Powder Indexing: User's Manual, The Lattice Press, 41 Guildford Park Avenue, Guildford, Surrey GU2 7NL, England, 2002.
- [20] P.E. Werner, Z. Krist. 120 (1964) 375.
- [21] A. Altomare, M.C. Burla, M. Carmalli, B. Carrozzini, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Rizzi, J. Appl. Crystallogr. 32 (1999) 339.
- [22] A. Altomare, M.C. Burla, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, J. Appl. Crystallogr. 28 (1995) 842.
- [23] A. Le Bail, H. Duroy, J. Fourquet, Mater. Res. Bull. 238 (1988) 447.
- [24] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
- [25] H.M. Rietveld, Acta Cryst. 22 (1967) 151.
- [26] A.C. Larson, R.B. von Dreele, GSAS: General Structure Analysis System, Los Alamos National Laboratory, 2000.
- [27] B.H. Toby, J. Appl. Cryst. 34 (2001) 210.
- [28] R.D. Shannon, Acta Cryst. A32 (1976) 751.
- [29] F.C. Palilla, A.K. Levine, M.R. Tomkus, J. Electrochem. Soc. 115 (1968) 642.
- [30] G. Blasse, Philips Res. Rep. 24 (1969) 131.
- [31] S.H.M. Poort, W.P. Blokpoel, G. Blasse, Chem. Mater. 7 (1995) 1547.
- [32] M. Kottaisamy, R. Jagannathan, P. Jeyagopal, R.P. Rao, R.L. Narayanan, J. Phys. D: Appl. Phys. 27 (1994) 2210.
- [33] D.L. Dexter, J. Chem. Phys. 21 (1953) 836.
- [34] L.G. van Uitert, J. Electrochem. Soc. 114 (1967) 1048.
- [35] L. Ozawa, P.M. Jaffe, J. Electrochem. Soc. 118 (1971) 1678.