Silicon-based oxynitride and nitride phosphors for white LEDs—A review

Rong-Jun Xie*, Naoto Hirosaki

Nitride Particle Group, Nano Ceramics Center, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Received 11 June 2007; received in revised form 25 July 2007; accepted 27 August 2007
Available online 23 October 2007

Abstract

As a novel class of inorganic phosphors, oxynitride and nitride luminescent materials have received considerable attention because of their potential applications in solid-state lightings and displays. In this review we focus on recent developments in the preparation, crystal structure, luminescence and applications of silicon-based oxynitride and nitride phosphors for white light-emitting diodes (LEDs). The structures of silicon-based oxynitrides and nitrides (i.e., nitridosilicates, nitridoaluminosilicates, oxonitridosilicates, oxonitridoaluminosilicates, and sialons) are generally built up of networks of crosslinking SiN₄ tetrahedra. This is anticipated to significantly lower the excited state of the 5d electrons of doped rare-earth elements due to large crystal-field splitting and a strong nephelauxetic effect. This enables the silicon-based oxynitride and nitride phosphors to have a broad excitation band extending from the ultraviolet to visible-light range, and thus strongly absorb blue-to-green light. The structural versatility of oxynitride and nitride phosphors makes it possible to attain all the emission colors of blue, green, yellow, and red; thus, they are suitable for use in white LEDs. This novel class of phosphors has demonstrated its superior suitability for use in white LEDs and can be used in bichromatic or multichromatic LEDs with excellent properties of high luminous efficacy, high chromatic stability, a wide range of white light with adjustable correlated color temperatures (CCTs), and brilliant color-rendering properties.

© 2007 NIMS and Elsevier Ltd. All rights reserved.

Keywords: Oxynitride; Nitride; Phosphor; Luminescence; White LEDs; Sialon

Contents

1. Introduction .......................................................................................................................... 589
2. Classification and crystal chemistry of nitride compounds .............................................. 589
3. Structure and luminescence of silicon-based oxynitride and nitride phosphors ............... 590
   3.1. Blue-emitting phosphors .............................................................................................. 590
   3.2. Green-emitting phosphors .......................................................................................... 592
   3.3. Yellow-emitting phosphors ........................................................................................ 594
   3.4. Red-emitting phosphors ............................................................................................. 595
4. Synthesis of silicon-based oxynitride and nitride phosphors ............................................. 597
   4.1. Solid-state reaction ..................................................................................................... 597
   4.2. Gas-reduction nitridation ............................................................................................ 597
   4.3. Carbothermal reduction and nitridation (CRN) .......................................................... 598
5. Applications of oxynitride and nitride phosphors in white LEDs ....................................... 598
6. Summary ............................................................................................................................... 599
Acknowledgments .................................................................................................................. 599
References ................................................................................................................................ 599

*Corresponding author. Tel.: +81 29 860 4312; fax: +81 29 851 3613.
E-mail address: Xie.Rong-Jun@nims.go.jp (R.-J. Xie).

1468-6996/$ - see front matter © 2007 NIMS and Elsevier Ltd. All rights reserved.
doi:10.1016/j.stam.2007.08.005
1. Introduction

Conventional incandescent or fluorescent lamps rely on either incandescence or discharge in gases. Both phenomena are associated with large energy losses that occur because of the high temperatures and large Stokes shifts involved. Light-emitting diodes (LEDs) using semiconductors offer an alternative method of illumination. The operation of LEDs is based on spontaneous light emission in semiconductors, which is due to the radiative recombination of excess electrons and holes [1] that are produced by the injection of current with small energy losses. Subsequently, the radiative recombination of the injected carriers may attain quantum yields close to unity. As a result, compared with conventional lamps, LED-based light sources have superior lifetime, efficiency, and reliability, which promise significant reductions in power consumption and pollution from fossil fuel power plants [1]. Currently, LEDs are widely used as indicators, rear lamps for vehicles, decorated lamps, backlights for cellular phones and liquid crystal displays, and small-area lighting. With advances in the brightness and color-rendering properties of LEDs, it is generally accepted that they will replace conventional lamps for general lighting in the near future.

In general, there are three methods of creating white light in LEDs: (i) using three individual monochromatic LEDs with blue, green, and red colors; (ii) combining an ultraviolet (UV) LED with blue, green, and red phosphors; and (iii) using a blue LED to pump yellow or green and red phosphors [2]. In the latter two cases, appropriate phosphors are used as downconversion luminescent materials. The excitation sources used for phosphors in LEDs differ greatly from those of phosphors in conventional lighting. The excitation sources for phosphors in LEDs are UV (360–410 nm) or blue light (420–480 nm), whereas those for conventional inorganic phosphors in cathode-ray tubes (CRTs) or fluorescent lamps are electron beams or mercury gas ($\lambda_{em} = 254$ nm). Therefore, the phosphors in LEDs should have high absorption of UV or blue light. In addition, they should also have the following characteristics: (i) high conversion efficiency; (ii) high stability against chemical, oxygen, carbon dioxide, and moisture; (iii) low thermal quenching; (iv) small and uniform particle size (5–20 $\mu$m); and (v) appropriate emission colors. The phosphor most commonly utilized in bichromatic white LEDs is the yellow-emitting (Y1) $\text{Ce}^{3+}$ (YAG:Ce) [1]. Other types of phosphor such as mercury gas (those for conventional inorganic phosphors in cathode-ray UV (360–410 nm) or blue light (420–480 nm), whereas lighting. The excitation sources for phosphors in LEDs are differ greatly from those of phosphors in conventional

2. Classification and crystal chemistry of nitride compounds

Nitride compounds are a large family of nitrogen-containing compounds that are formed by combining nitrogen with less electronegative elements. Generally, nitrides can be grouped into three types: (i) metallic, (ii) ionic, and (iii) covalent compounds, based on the chemical characteristics of the bonds between nitrogen and other elements [15]. Metallic nitrides, such as TiN, ZrN, VN, CrN, and FeN, are usually produced by combining nitrogen with transition metals. Ionic nitrides are usually of the form of M–N, with M being an alkali-, alkaline-earth and wide band gaps, whereas metallic and ionic nitrides are either electrical or ionic conductors and both have narrow band gaps. Furthermore, the covalent chemical bonding in nitrides gives rise to a strong nephelauxetic effect (i.e., electron cloud expansion), reducing the energy of the excited state of the 5d electrons of the activators (e.g., $\text{Eu}^{2+}$, $\text{Ce}^{3+}$) [16–20]. This results in long excitation/emission wavelengths and low thermal quenching, which cannot be achieved in conventional phosphors used in lamps and CRTs.
Alternatively, nitride compounds can also be divided into the following groups depending on the number of elements included: (i) binary, (ii) ternary, (iii) quaternary, and (iv) multinary. Binary covalent nitrides, such as GaN, BN, and AlN, cannot be easily considered as host lattices for phosphors in white LEDs because they do not have suitable crystal sites for activators [13], although some of them show interesting luminescence properties in thin-film form [7–10]. The ternary, quaternary, and multinary covalent nitride compounds, typically silicon-based nitrides, are interesting because of their unique and rigid crystal structures, availability of suitable crystal sites for activators, and their structural versatility, which enable the doping of rare-earth ions to provide useful photoluminescence.

Schneck and coworkers [21–28] extensively investigated the preparation and crystal structures of silicon-based oxynitride and nitride compounds. A new class of materials consisting of nitridosilicates, nitridoaluminosilicates, and sialons is formed by the integration of nitrogen in silicates or aluminosilicates. Compared with the well-known oxosilicates, the newly developed nitrides exhibit a much wider range of structural complexity and flexibility, forming a large family of multiterminal compounds. In addition to these nitride compounds, oxynitrides (i.e., oxonitridosilicates and oxonitridoaluminosilicates) are derived from oxosilicates and oxoaluminosilicates by exchanges of oxygen with nitrogen and of silicon with aluminum, respectively. Therefore, similar to oxosilicates, the structures of silicon-based oxynitride and nitride compounds are generally built up of highly condensed networks constructed from linked SiX₄ (X = O, N) tetrahedra. The degree of condensation in the network of Si₅ tetrahedra is simply evaluated by the ratio of tetrahedral Si centers to bridging atoms X. In oxosilicates the Si:X ratio reaches a maximum of 0.5 in SiO₂, while in nitrides the Si:X ratio may vary in a broad range of 0.25–0.75. This indicates that nitrides have a high degree of condensation due to the fact that the structural possibilities in oxosilicate lattices are limited to terminal oxygen atoms and simple bridging O[2] atoms, whereas the nitrogen atoms in nitrides are generally connected with two (N[3]), three (N[4]), or even four (N[4]) silicon atoms as in BaSi₅N₁₀ [23] and MYbSi₄N₇ (M = Sr, Ba) [24,25]. Consequently, the highly condensed SiN₄-based networks and the high stability of the chemical bonding between the constituent elements result in the extraordinary chemical and thermal stability of silicon-based oxynitride and nitride materials.

3. Structure and luminescence of silicon-based oxynitride and nitride phosphors

Compared with oxide-, boride-, sulfide-, or phosphate-based phosphors, the study of oxynitride and nitride phosphors is at a very early stage. The possibility of realizing white LEDs has greatly catalyzed the research and development of oxynitride and nitride phosphors, and they are receiving significant attention from both scientists and engineers. For rare-earth ions (i.e., Eu²⁺ and Ce³⁺) with the 5d electrons unshielded from the crystal field by the 5s and 5p electrons when in the excited state, the spectral properties are strongly affected by the surrounding environment (e.g., symmetry, covalence, coordination, bond length, site size, crystal-field strength, etc.). Because of the higher formal charge of N³⁻ compared with O²⁻ and the nephelauxetic effect (covalence), the crystal-field splitting of the 5d levels of rare earths is larger and the center of gravity of the 5d states is shifted to lower energies (i.e., longer wavelength) than in an analogous oxygen environment. Consequently, silicon-based oxynitride and nitride phosphors are anticipated to show longer excitation and emission wavelengths than their oxide counterparts. Furthermore, the Stokes shift becomes smaller in a rigid lattice with a more extended network of SiN₄ tetrahedra. A small Stokes shift leads to high conversion efficiency and small thermal quenching of phosphors.

A variety of oxynitride and nitride materials with promising luminescent properties have been discovered recently [11–14,16–19,29–43]. In this section, we will review the structure and luminescence of these rare-earth-doped oxynitride and nitride phosphors.

3.1. Blue-emitting phosphors

A blue-emitting phosphor must be combined with green and red phosphors to create white light when UV or near ultraviolet (NUV) LED is used. Although a large number of oxide-based phosphors emit an intense blue color under UV or NUV light excitation, the high thermal quenching or thermal degradation is a serious problem if they are used in white LEDs (e.g., BaMgAl₁₀O₁₇:Eu²⁺ [44]). Ce³⁺- or Eu³⁺-activated oxynitride blue phosphors undergo little thermal degradation and have strong absorption of UV or NUV light, enabling them to be alternative candidates for white LEDs. In the following, three types of blue-emitting oxynitride phosphor (i.e., LaAl(Si₆₋ₓAlₓ)N₁₀₋ₓOₓ:Ce³⁺, z-sialon:Ce³⁺, and (Y,La)-Si–O–N:Ce³⁺) will be described.

The preparation and crystal structure of a JEM phase with chemical formula LaAl(Si₆₋ₓAlₓ)N₁₀₋ₓOₓ was reported by Grins et al. [45]. JEM has an orthorhombic structure (space group Pbnm) with a = 9.4303 Å, b = 9.7689 Å, and c = 8.9386 Å. The Al atoms and (Si, Al) atoms are tetrahedrally coordinated by (N, O) atoms, yielding an Al(Si,Al)O₃ network (see Fig. 1). The La atoms are accommodated in tunnels extending along the [001] direction and are irregularly coordinated by seven (N, O) atoms at an average distance of 2.70 Å. Hirotsuki et al. [11] reported the luminescence of Ce³⁺-doped JEM. As shown in Fig. 2, the emission spectrum of JEM:Ce³⁺ displays a broad band extending from 400 to 700 nm under 368 nm excitation, with a peak located at 475 nm. The broad excitation spectrum extending from 200 to 450 nm is due to the 4f→5d electronic transition of Ce³⁺. Both spectra are redshifted when the concentration of Ce³⁺ or the z value increases, enabling this blue phosphor


The \( \alpha \)-sialon is a solid solution of \( \alpha \)-Si\(_3\)N\(_4\) and is formed by the partial replacement of Si–N bonds with Al–N and Al–O bonds. The general formula of \( \alpha \)-sialon, consisting of four “Si\(_3\)N\(_4\)” units, can be given as \( \text{M}_{x} \text{Si}_{12-m-n} \text{Al}_{m+n} \text{O}_{n} \text{N}_{16-n} \) (\( x \) is the solubility of the M metal) [46–48], where \( m \) and \( n \) are the numbers of Al–N and Al–O bonds substituting for Si–N bonds, respectively. The charge discrepancy caused by the substitution is compensated for by the introduction of the M cations including Li\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Y\(^{3+}\), and some lanthanides. It has a hexagonal crystal structure and the \( P3_1c \) space group. In the structure of \( \alpha \)-sialon, the M cations occupy the interstitial sites and are coordinated by seven (N, O) anions [49].

The \( \text{Ce}^{3+}\)-activated \( \alpha \)-sialon (Ca\(_{0.898}\)Ce\(_{0.068}\)Si\(_9\)Al\(_3\)ON\(_{15}\)) shows blue emission, as shown in Fig. 4. The emission spectrum, centered at 495 nm, extends from 400 to 650 nm upon 389 nm excitation. The peak emission wavelength is redshifted from 485 to 503 nm when the Ce concentration increases from 5 to 25 mol\% [29,30]. Moreover, the emission of \( \alpha \)-sialon:Ce\(^{3+}\) can also be tuned by varying the values of \( m \) and \( n \). The excitation spectrum shows a broad band with a peak located at 389 nm, which closely matches the emission wavelengths of UV or NUV LEDs.

There are several compounds in Y–Si–O–N and La–Si–O–N systems, and their luminescence spectra have been reported recently [17,31]. Van Krevel et al. [17] investigated the luminescent properties of Ce\(^{3+}\)-doped Y–Si–O–N oxynitride compounds. Generally, these compounds emit a blue color with a peak emission wavelength of 400–500 nm and show maximum excitation bands at
325–400 nm. They demonstrated that the N/O ratio and the crystal structure had a strong effect on the emission, Stokes shift, and crystal-field splitting. Larger N/O ratios and stiffer structures led to longer-wavelength emissions, smaller Stokes shifts, and larger crystal-field splitting [17]. A similar tendency was observed in Ce³⁺-doped La–Si–O–N materials [31]. We have studied the emission of Ce³⁺ in La–Si–O–N compounds with different structures: La₅Si₃O₁₂N (hexagonal), LaSiO₂N (hexagonal), and La₅Si₅O₂N₁₁ (orthorhombic), and have shown that La₅Si₅O₂N₁₁ has encouraging luminescent properties for white LEDs. Fig. 5 shows the structure of La₅Si₅O₂N₁₁, which contains ribbons as structural units with a composition of Si₆(O,N)₁₄. The ribbons extend along the [010] direction and are formed by corner-sharing Si(O,N)₄ tetrahedra. The La₁ atom is octahedrally coordinated by 4 O/N and 2 O atoms, and the La2 atom is coordinated by 5 O/N, 2 O atoms, and 1 N atom, which approximately form a cubic antiprism [50]. Fig. 6 shows the excitation and emission spectra of Ce³⁺-doped La–Si–O–N materials. It reveals that the peak excitation band of La–Si–O–N:Ce³⁺ is around 360 nm, and those of La₄.₉Ce₀.₁Si₃O₁₂N, La₀.₉₆Ce₀.₀₄SiO₂N, and La₂.₈₂Ce₀.₁₈Si₈O₄N₁₁ are 472, 416, and 425 nm, respectively. We have also investigated the temperature dependence of the luminescence of Ce³⁺-doped La–Si–O–N materials and observed that La₅Si₅O₂N₁₁:Ce has the lowest thermal quenching because it has the densest structure and highest N/O ratio [31].

3.2. Green-emitting phosphors

A green-emitting phosphor is used in the case when white LEDs utilize a UV-, NUV-, or blue LED as the primary lighting source. Rare-earth-doped oxynitride and nitride green phosphors highly suitable for use in white LEDs have been reported in the literature [25,32–36], and they are reviewed below.

Hirosaki et al. [32] reported a green oxynitride phosphor based on Eu²⁺-doped β-sialon. β-Sialon is structurally derived from β-Si₃N₄ by the equivalent substitution of

![Fig. 5. Crystal structure of La₅Si₅O₂N₁₁ viewed along the [001] direction. The blue, green, pale blue, red, and gray spheres represent La, N, O, Si, and O/N atoms, respectively.](image)

![Fig. 6. Excitation (a) and emission (b) spectra of La₄.₉Ce₀.₁Si₃O₁₂N, La₀.₉₆Ce₀.₀₄SiO₂N, and La₂.₈₂Ce₀.₁₈Si₈O₄N₁₁.](image)
Al–O for Si–N, and its chemical composition can be written as Si$_{6-z}$Al$_z$O$_{0.5}$N$_{7.5}$ ($z$ represents the number of Al–O pairs substituting for Si–N pairs, and $0<z\leq 4.2$). β-Sialon has a hexagonal crystal structure and the P6$_3$ or P6$_5$/m space group [51,52]. In this structure there are continuous channels parallel to the c direction (see Fig. 7). The β-sialon:Eu$^{2+}$ phosphor produces intense green emission with a peak located at 538 nm, as can be seen in Fig. 8. The broad emission spectrum has a full-width at half-maximum of 55 nm. Two well-resolved broad bands centered at 303 and 400 nm are observed in the excitation spectrum. The broad excitation range enables the β-sialon:Eu$^{2+}$ phosphor to emit strongly under NUV (400–420 nm) or blue (420–470 nm) light excitation. Xie et al. [33] investigated the effects of the $z$-value and the Eu$^{2+}$ concentration on the phase formation and luminescent properties of β-sialon:Eu$^{2+}$ phosphors. The results showed that (i) the samples with lower $z$-values ($z<1.0$) had higher phase purity, a smaller and more uniform particle size, and produced greater emission; (ii) the optimal Eu$^{2+}$ concentration was about 0.3 mol%. In addition, the β-sialon:Eu$^{2+}$ phosphor showed low thermal quenching; its emission intensity at 150 °C was 86% of that measured at room temperature [33].

Xie et al. [34] reported the green emission of Yb$^{2+}$ in Ca-$\alpha$-sialon. As can be seen in Fig. 9, the excitation spectrum shows a broad band centered at 445 nm, and the peak emission wavelength is about 550 nm upon blue-light excitation. The emission of Yb$^{2+}$, arising from the transition 4f$^1$5d$\rightarrow$4f$^2$, usually occurs between 360 and 450 nm, as has been shown for halides, fluorides, sulphates, and phosphates [53–55]. However, luminescence occurs at low energies in Ca-$\alpha$-sialon, which can principally be ascribed to the large crystal-field splitting and the strong nephelauxetic effect induced as a result of the nitrogen-rich coordination of Yb$^{2+}$ in $\alpha$-sialon. A much longer wavelength emission of Yb$^{2+}$ in SrSi$_2$O$_2$N$_2$ was observed at 562 nm by Bachmann et al. [56].

MSi$_2$O$_2$N$_2$ compounds crystallize in a monoclinic lattice with different space groups and lattice parameters for M = Ca, Sr, and Ba: CaSi$_2$O$_2$N$_2$ (P2$_1$/c), SrSi$_2$O$_2$N$_2$ (P2$_1$/m), and BaSi$_2$O$_2$N$_2$ (P2/m) [25,35]. CaSi$_2$O$_2$N$_2$ and SrSi$_2$O$_2$N$_2$ are structurally related, both representing a new class of layered materials with layers of (Si$_2$O$_2$N$_2$)$_2$ that consist of SiON$_3$ tetrahedrons. The N atom bridges three Si atoms, while the O atom is bound terminally to the Si atom. There are four types of site for the M$^{2+}$ ions, each surrounded by six oxygen atoms in the form of a distorted trigonal prism. The excitation and emission spectra of Eu$^{2+}$-doped MSi$_2$O$_2$N$_2$ materials are given in Fig. 10. As can be seen, CaSi$_2$O$_2$N$_2$:Eu$^{2+}$ shows a yellowish emission with a maximum intensity at 562 nm, SrSi$_2$O$_2$N$_2$:Eu$^{2+}$ emits a green color with a maximum intensity at 543 nm, and BaSi$_2$O$_2$N$_2$:Eu$^{2+}$ yields blue-green emission with a peak at 491 nm. These results were also observed by Li et al. [35]. The excitation spectrum of CaSi$_2$O$_2$N$_2$:Eu$^{2+}$ shows a flat and broad band extending from 300 to 450 nm, while there are two well-resolved broad bands centered at 300 and 450 nm.
450 nm in the excitation spectra of SrSi$_2$O$_2$N$_2$:Eu$^{2+}$ and BaSi$_2$O$_2$N$_2$:Eu$^{2+}$, respectively.

MYSi$_4$N$_7$ (M = Sr, Ba) are quaternary nitride compounds. The structure of MYSi$_4$N$_7$ consists of SiN$_4$ tetrahedra that share corners forming a three-dimensional network structure with large channels along the [1 0 0] and [0 1 0] directions formed by Si$_6$N$_6$ rings [36,57], as shown in Fig. 11. Both Sr$^{2+}$ and Y$^{3+}$ ions occupy a site in these channels. The Sr$^{2+}$ ion is coordinated by 12 nitrogen atoms (SrN$_{12}$) and the Y$^{3+}$ ion is coordinated by six nitrogen atoms (YN$_6$). Li et al. [36] investigated the luminescent properties of Eu$^{2+}$-doped MYSi$_4$N$_7$ (M = Sr, Ba) materials, and observed green emission when they were excited by NUV light ($\lambda_{ex} = 390$ nm). The emission of MYSi$_4$N$_7$:Eu$^{2+}$ occurred at 503–527 nm for M = Ba and at 548–570 nm for M = Sr. The relatively short wavelength emission of Eu$^{2+}$ in this nitride is ascribed to the longer bond length of Eu–N ($\bar{r}$ = 3.011 Å) than that of $\alpha$-sialon ($\bar{r}$ = 2.605 Å) [49].

### 3.3. Yellow-emitting phosphors

The first commercially available white LED was fabricated in 1996 by using a yellow-emitting (Y$_{1-x}$Gd$_x$)$_3$(Al$_{1-y}$Ga$_y$)$_5$O$_{12}$ phosphor and a GaN-based blue-LED chip. The principle of this white LED is that part of the blue light from the LED chip is converted to yellow light by YAG:Ce$^{3+}$, and the resulting mix of blue and yellow light has the appearance of white light. This white LED cannot create warm white light because the YAG phosphor cannot produce red emission. Moreover, the thermal quenching of the YAG phosphor is high and strongly related to its composition, leading to changes in the chromaticity of the white LED when it is used. Therefore, it is essential to develop novel yellow phosphors that emit an orangish-yellow color and undergo low thermal quenching.

Xie et al. [19,30,37,39,40] systematically studied the luminescent properties of Eu$^{2+}$-doped Ca-$z$-sialon phosphors, and observed a bright yellow-orange color when they were excited by blue light. Fig. 12 shows the typical excitation and emission spectra of Eu$^{2+}$-doped Ca-$z$-sialon. This phosphor has a broadband emission spectrum extending from 500 to 750 nm, with a peak located at 581 nm. The excitation spectrum shows two broad bands centered at 300 and 420 nm and a shoulder at 450 nm. The fact that the emission wavelength is longer than that of YAG:Ce (550–570 nm) implies that warm white light can be produced by combining Ca-$z$-sialon:Eu$^{2+}$ and a blue-LED chip. In addition, the yellow emission of Ca-$z$-sialon:Eu$^{2+}$ can be tuned by substituting Ca with other metals such as Li, Mg, and Y, and can even be adjusted by tailoring the composition of the host lattice by changing the values of $m$ and $n$ in the chemical formula [39,40,58,59]. Of particular interest is Li-$z$-sialon:Eu$^{2+}$,
which emits a yellow–green color, making it possible to generate daylight light when combined with a blue LED. This indicates that warm-white-to-daylight light can be realized using a single α-sialon:Eu\(^{2+}\) yellow phosphor with different emission colors. Furthermore, we have demonstrated that the α-sialon:Eu\(^{2+}\) phosphor has lower thermal quenching than YAG:Ce\(^{3+}\), as shown in Fig. 13. The low thermal quenching is expected to lead to a small variation of chromaticity in white LEDs using α-sialon:Eu\(^{2+}\).

### 3.4. Red-emitting phosphors

A red-emitting phosphor is usually combined with green and/or blue phosphors in the case of white LEDs utilizing a UV-, NUV-, or blue-LED chip. The search for red phosphors for use in white LEDs has been mostly concentrated on Eu\(^{3+}\)-doped materials (e.g., NaEu(W, Mo)\(_2\)O\(_8\) [60]), and Eu\(^{2+}\)-doped sulfides (e.g., CaS:Eu\(^{2+}\) [5]). However, these phosphors have either low absorption in the blue-light range (i.e., oxides) or low chemical stability (i.e., sulfides). It is therefore necessary to develop red phosphors with high chemical stability and high emission efficiency upon blue-light excitations. Previous studies demonstrated that silicon-based nitride compounds are good host lattices for red luminescent materials [16,41–43], and they are described in the following.

Schnick et al. [26,27] reported the crystal structures of single crystals of M\(_2\)Si\(_5\)N\(_8\) (M = Ca, Sr, Ba). Ca\(_2\)Si\(_5\)N\(_8\) has a monoclinic crystal system with the space group of Cc, whereas both Sr\(_2\)Si\(_5\)N\(_8\) and Ba\(_2\)Si\(_5\)N\(_8\) have an orthorhombic lattice with the space group of \(Pmn_2_1\). The local coordination in the structures is similar for these ternary alkaline-earth Si\(_3\)N\(_4\)'s; half the nitrogen atoms are connected to two Si neighbors and the other half have three Si neighbors. Each Ca atom in Ca\(_2\)Si\(_5\)N\(_8\) is coordinated to seven nitrogen atoms, while Sr in Sr\(_2\)Si\(_5\)N\(_8\) and Ba in Ba\(_2\)Si\(_5\)N\(_8\) are coordinated to eight or nine nitrogen atoms (see Fig. 14). The average bond length between alkaline-earth metals and nitrogen is about 2.880 Å. The luminescence of Eu\(^{2+}\)-doped Ba\(_2\)Si\(_5\)N\(_8\) was reported by Hoppe et al. [16], and that of Eu\(^{2+}\)-doped M\(_2\)Si\(_5\)N\(_8\) (M = Ca, Sr, Ba) was later reported by Li et al. [41]. The red emission in M\(_2\)Si\(_5\)N\(_8\):Eu\(^{2+}\) was attributed to the large crystal-field splitting and strong nephelauxetic effect. The red phosphor emits an intense orange-red or red color, depending on the alkaline-earth metal. The peak emission wavelength shifts upward with increasing ionic size of the alkaline-earth.

![Fig. 12. Excitation and emission spectra of Ca\(_{0.925}\)Eu\(_{0.075}\)Si\(_9\)Al\(_3\)O\(_{15}\). The excitation and monitoring wavelengths are 420 and 581 nm, respectively.](image)

![Fig. 13. Temperature dependence of emission intensities of Ca-α-sialon:Eu\(^{2+}\) and YAG:Ce\(^{3+}\).](image)

![Fig. 14. Crystal structure of Sr\(_2\)Si\(_5\)N\(_8\) viewed along the \([0 0 1]\) direction. The blue, red, and green spheres represent Sr, Si, and N atoms, respectively.](image)
metal, and it is 623, 640, and 650 nm for Ca$_2$Si$_5$N$_8$:Eu$^{2+}$, Sr$_2$Si$_5$N$_8$:Eu$^{2+}$, and Ba$_2$Si$_5$N$_8$:Eu$^{2+}$, respectively [14,41]. The excitation and emission spectra of these phosphors resemble each other. Fig. 15 shows typical luminescence spectra of Sr$_2$Si$_5$N$_8$:Eu$^{2+}$. The broad excitation spectrum centered at 450 nm markedly shifts to the long-wavelength side and covers the visible-light range. The temperature dependence of the emission intensity of Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ is given in Fig. 16. The PL intensity measured at 150 °C is 86% of that measured at room temperature, indicative of low thermal quenching [61].

Uheda et al. [42] reported an alternative red phosphor with formula CaAlSiN$_3$:Eu$^{2+}$. CaAlSiN$_3$ has an orthorhombic crystal structure and the space group of Cmc$_2$$_1$ with unit cell parameters $a = 9.8007$ Å, $b = 5.6497$ Å, and $c = 5.0627$ Å. The structure of CaAlSiN$_3$ is built up of (Si/Al)N$_4$ tetrahedra linked in a three-dimensional structure: one-third of the nitrogen atoms (N2) are linked with two Si/Al neighbors and the remaining two-thirds (N1) are connected with three Si/Al neighbors (see Fig. 17). The Al and Si atoms are randomly distributed on the same tetrahedral sites and are connected with N atoms to form vertex-linked M6N18 rings (M = Al, Si). The Ca atom, residing in the tunnels surrounded by six corner-sharing tetrahedra of (Si/Al)N$_4$, is coordinated to two four nitrogen atoms with an average distance of 2.451 Å. CaAlSiN$_3$:Eu$^{2+}$ is a red phosphor, and its luminescence spectra are given in Fig. 18. Both the excitation and emission spectra of CaAlSiN$_3$:Eu$^{2+}$ are very similar to those of M$_2$Si$_5$N$_8$:Eu$^{2+}$. The excitation spectrum is extremely broad and covers the range of 250–600 nm, closely matching the emission wavelength of NUV or blue LEDs. A broad emission band centered at 650 nm is observed upon 450 nm excitation, and it can be tuned by substituting Ca with other metals or by controlling the Eu$^{2+}$ concentration [42]. The emission intensity of
CaAlSiN₃:Eu²⁺ at 150 °C is about 89% of that measured at room temperature (see Fig. 16).

Le Toquin et al. [43] reported another nitride host lattice for red phosphors with formula CaSiN₂. Crystals of CaSiN₂ were prepared and the structure was determined by Ottinger et al. [62] and Gal et al. [63] independently. CaSiN₂, which is isostructural with KGaO₂, crystallizes in an orthorhombic structure with the space group Pnma and cell parameters a = 5.1229 Å, b = 10.2074 Å, and c = 14.8233 Å. There are two sites for Ca atoms. Ca₁ is surrounded by four N atoms with distances of 2.40–2.49 Å and by two further N atoms to form an approximately octahedral geometry. Ca₂ is in a highly distorted octahedral environment, again with four shorter Ca–N distances (between 2.43 and 2.48 Å) and two longer distances of approximately 2.8 Å. All the nitrogen atoms in CaSiN₂ are at the shared vertexes of a pair of structures and are coordinated to two Si atoms (see Fig. 19). By doping CaSiN₂ with Eu²⁺ or Ce³⁺, broad red emission bands were observed by Le Toquin et al. [43]. The maximum emission was at 605 and 625 nm, and the maximum excitation was at 400 and 535 nm for CaSiN₂:Eu²⁺ and CaAlSiN₃:Eu²⁺, respectively. The excitation and emission of CaSiN₂:Ce³⁺ can be adjusted by the partial substitution of Ca with Mg or Sr or that of Si with Al. All the nitrogen atoms in CaSiN₂ are at the shared vertexes of a pair of structures and are coordinated to two Si atoms (see Fig. 19). By doping CaSiN₂ with Eu²⁺ or Ce³⁺, broad red emission bands were observed by Le Toquin et al. [43]. The maximum emission was at 605 and 625 nm, and the maximum excitation was at 400 and 535 nm for CaSiN₂:Eu²⁺ and CaAlSiN₃:Eu²⁺, respectively. The excitation and emission of CaSiN₂:Ce³⁺ can be adjusted by the partial substitution of Ca with Mg or Sr or that of Si with Al. The external quantum efficiency of CaSiN₂:Ce³⁺ was reported to be 40% [43].

4. Synthesis of silicon-based oxynitride and nitride phosphors

Phosphors for white LEDs are usually in powder form. The phosphor powders are commonly synthesized by solid-state-reaction, gas-phase, or solution (i.e., wet chemistry) methods. For nitride phosphors, which differ from oxide-based ones in that they contain nitrogen, nitride starting powders or nitrogen-containing sources, are there-}

fore frequently utilized during their preparation. In this sense, the synthetic route to nitride phosphors, such as silicon-based multinary oxynitride and nitride phosphors, is therefore very limited. Up to now, three major approaches have been used to synthesize oxynitride and nitride phosphors: a solid-state reaction, gas-reduction nitridation (GRN), and carbothermal reduction nitridation (CRN).

4.1. Solid-state reaction

The solid-state reaction is a common and simple method of synthesizing oxynitride and nitride phosphor powders. It usually involves reactions at high temperatures among powder precursors containing the corresponding chemical constituents. Si₃N₄ powder is a commonly used starting material for the synthesis of multinary silicon-based oxynitrides and nitrides. Because of the chemical inertness of Si₃N₄, the synthesis of nitride phosphors is usually carried out at high temperatures (i.e., 1500–2000 °C). The more reactive silicon diimide (Si(NH)₂) was used instead of Si₃N₄ to synthesize nitridosilicate phosphors by Schnick and coworkers [16,26,27]. Other starting materials may include metals (e.g., Ca, Sr, Ba, Eu), metal nitrides (e.g., AlN, Ca₃N₂, EuN), or metal oxides (e.g., Al₂O₃, CaCO₃, Li₂CO₃, Ln₂O₃). At the same time, a nitrogen atmosphere under pressures in the range of 0.1–1.0 MPa is required to protect the powder from oxidation or decomposition.

We have applied the solid-state reaction to prepare oxynitride and nitride phosphors including α-sialon:Eu²⁺, β-sialon:Eu³⁺, JEM:Ce³⁺, La–Si–O–N:Ce³⁺, Sr₂Si₅N₈:Eu²⁺, and CaAlSiN₃:Eu²⁺. A gas-pressure sintering furnace with a graphite heating element was used. For example, CaAlSiN₃:Eu²⁺ was formed by the following reaction among metal nitride starting powders at 1600 °C under a 1.0 MPa N₂ atmosphere:

\[
\text{Si}_3\text{N}_4 + \text{AlN} + \text{Ca}_3\text{N}_2 + \text{EuN} \rightarrow \text{CaAlSiN}_3 : \text{Eu}.
\]

In addition, Hoppe et al. [16] used a high-frequency furnace to synthesize Ba₂Si₅N₈:Eu²⁺ red phosphors through the following reaction between metal Ba and silicon diimide at 1500–1650 °C under a nitrogen atmosphere:

\[
2\text{Ba} + \text{Eu(NH)}_2 \rightarrow \text{Ba}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+} + \text{N}_2 + 5\text{H}_2.
\]

4.2. Gas-reduction nitridation

The phosphor powders prepared by the solid-state reaction usually consist of hard agglomerates and have a large particle size and broad size distribution. It is essential to pulverize the fired products to obtain fine and well-dispersed powders, and this process damages the surface of particles and hence reduces the luminescence. In addition, some precursors such as metals or nitrides are sensitive to air and expensive, resulting in complex and multistep processing. Therefore, it is necessary to develop an
alternative method in order to obtain fine powders, simplify the process, and reduce the cost.

GRN is an effective and cheap method of synthesizing oxynitride and nitride phosphors. In this approach, the reaction is generally performed in an alumina boat containing the oxide precursor powder loaded inside an alumina/quartz tube through which NH3 or NH3–CH4 gas flows at appropriate rates at high temperatures (1300–1600 °C). The NH3 or NH3–CH4 gas acts as both reducing and nitriding agents. For example, Suehiro et al. [64] used GRN to prepare submicron-sized α-sialon:Eu2+ powders (~300 nm) at a temperature 200 °C lower than that used in the solid-state reaction. The precursor was a powder in the CaO–SiO2–Al2O3 system. The effects of processing parameters such as heating rate, flow rate, volume ratio of gases, temperature, and holding time were investigated later by Li et al. [65]. Gal et al. [63] synthesized CaSiN2 using CaSi as the precursor powder and NH3 as the nitriding agent through the following reaction [63]:

\[
\text{CaSi} + 2\text{NH}_3 \rightarrow \text{CaSiN}_2 + 2\text{H}_2.
\]

4.3. Carbothermal reduction and nitridation (CRN)

CRN is also a cheap method of synthesizing silicon-based oxynitride and nitride compounds [66]. It differs from GRN in that (i) carbon powder is applied as the reducing agent and (ii) N2 instead of NH3 or NH3–CH4 is used as the nitriding agent. The precursor for CRN is a mixture of oxide, nitride and carbon powders. Zhang et al. [67] prepared α-sialon:Eu2+ (Ca1-xEu_xSi10Al2N16) powders by firing a mixture of Si3N4, CaCO3, Al2O3, Eu2O3, and C powders at 1600 °C in flowing N2. α-Sialon:Eu2+ was formed via the following chemical reaction [68]:

\[
\text{Si}_3\text{N}_4 + \text{CaO} + \text{Al}_2\text{O}_3 + \text{Eu}_2\text{O}_3 + \text{C} + \text{N}_2 \rightarrow \text{CaSi}_{10}\text{Al}_2\text{N}_{16} : \text{Eu} + \text{CO}_2.
\]

The α-sialon:Eu2+ phosphor emitted yellow emission with a band centered at 585–605 nm, which is consistent with that prepared by the solid-state reaction. CRN was also utilized to prepare the Sr2Si5N8:Eu2+ phosphor by heating a mixture of Si3N4, SrCO3, Eu2O3, and C powders at 1500 °C through the following reaction:

\[
\text{Si}_3\text{N}_4 + \text{SrO} + \text{Eu}_2\text{O}_3 + \text{C} + \text{N}_2 \rightarrow \text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu} + \text{CO}_2.
\]

The residual carbon in powders prepared by CRN can be removed by post-annealing the phosphor powders in a carbon-free atmosphere (e.g., N2) at 1600 °C.

5. Applications of oxynitride and nitride phosphors in white LEDs

As shown in the previous section, oxynitride and nitride phosphors emit visible blue, green, yellow, and red light efficiently under UV and/or visible-light irradiation. This closely matches the emission wavelengths of UV-, NUV-, or blue-LED chips, enabling their use as downconversion phosphors in white LEDs. The fabrication of both bichromatic and multichromatic white LEDs has been attempted by combining silicon-based oxynitride and nitride phosphors with a blue-LED chip [11,12,39,40, 69–75]. Table 1 shows a summary of the optical properties of white LEDs prepared by combining silicon-based oxynitride and nitride phosphor(s) with a blue-LED chip.

The first bichromatic white LED using an oxynitride phosphor was reported by Sakuma and coworkers [11,12,69,70]. They fabricated a white LED by combining an orangish-yellow α-sialon:Eu2+ phosphor (λem = 586 nm) with a blue-LED chip (λem = 450 nm). A warm white LED with a correlated color temperature (CCT) of about 2750 K was produced. Furthermore, Sakuma et al. [69] showed that the chromaticity coordinates of white LEDs using Ca-α-sialon:Eu2+ varied from (0.503, 0.463) to (0.509, 0.464), whereas those of LEDs using YAG:Ce3+ shifted significantly from (0.393, 0.461) to (0.383, 0.433) when they were measured at 200 °C. The high stability of the chromaticity coordinates is due to the low thermal quenching of α-sialon:Eu2+. By tuning the emission wavelength of α-sialon:Eu2+ through tailoring the composition, Xie and coworkers [39,40] demonstrated that white-to-daylight white LEDs could also be realized using a single short-wavelength Li-α-sialon:Eu2+ phosphor. The luminous efficacy of these white LEDs was 40–55 lm/W, about

Table 1
Examples of white LEDs utilizing silicon-based oxynitride and nitride phosphors

| Blue LEDs + phosphors | Color temperature (K) | Average color-rendering index | Luminous efficacy (lm/W) | Reference |
|-----------------------|-----------------------|-------------------------------|-------------------------|-----------|
| Yellow                | Green                 | Red                           |                         |           |
| Ca-α-sialon:Eu        | –                     | –                             | 2600–3100               | 57        | 26, 42, 51, 55 | [11,12,69,70] |
| Li-α-sialon:Eu        | –                     | –                             | 3000–6150               | 63–74     | 40–44, 46–55  | [39,40]    |
| Ca-α-sialon:Eu        | α-sialon:Eu           | CaAlSiN1.5:Eu                 | 2780–6850               | 84–90     | 26–35         | [11,12,70] |
| –                    | Ca-α-sialon:Yb        | SrSi2N2:Eu                    | 2700–6700               | 82–83     | 17–23         | [72]       |
| –                    | SrSi2O3:Eu            | SrSi2N2:Eu                    | 3200                    | 90        | 25*           | [73]       |
| –                    | SrSi2O3:Eu            | CaSiN2:Eu                     | 5206                    | 90.5      | 30             | [74]       |

*The luminous efficacy was measured at 1 W input (35 mA). Other data were measured at 20 mA.
2 times higher than that of incandescent lamps. The color-rendering index (CRI) of the bichromatic white LEDs using α-sialon:Eu<sup>2+</sup> was \( \text{Ra} = 55–72 \), which is acceptable for some applications such as backlights, flashlights, and car interior lighting.

To improve the color-rendering properties of white LEDs for general illumination, multichromatic white LEDs have been prepared using phosphor blends. Sakuma et al. [70] fabricated white LEDs by combining β-sialon:Eu<sup>2+</sup>, α-sialon:Eu<sup>2+</sup>, and CaAlSiN<sub>3</sub>:Eu<sup>2+</sup> with a blue-LED chip. The CRI value of the white LED (CCT = 2840 K) was \( \text{Ra} = 81–88 \), and the luminous efficacy was 24–28 lm/W. Later, Kimura et al. [71] added a bluish-green BaSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub>:Eu<sup>2+</sup> phosphor into the above phosphor mixture and obtained ultrahigh color rendering and high-efficiency white LEDs (\( \text{Ra} = 95–98 \), 28–35 lm/W). Xie et al. [72] used α-sialon:Yb<sup>2+</sup> and SrSi<sub>2</sub>N<sub>2</sub>:Eu<sup>2+</sup> phosphors as well as a blue LED to fabricate white LEDs. The CRI and luminous efficiency of these white LEDs were \( \text{Ra} = 82–83 \) and 17–23 lm/W, respectively. Mueller-Mach et al. [73] reported highly efficient white LEDs with \( \text{Ra} = 90 \), using the phosphor blend of Sr<sub>2</sub>SiN<sub>2</sub>:Eu<sup>2+</sup> and SrSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub>:Eu<sup>2+</sup>. Recently, Yang et al. [74] have reported white LEDs using SrSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub>:Eu<sup>2+</sup> and CaSiN<sub>2</sub>:Ce<sup>3+</sup>, which showed a luminous efficacy of 30 lm/W and a CRI of \( \text{Ra} = 92 \).

In addition, oxynitride/nitride phosphors were used in combination with NUV LED chips to generate white light by Takahashi et al. [75]. White LEDs were prepared by pumping the phosphor blend of JEM:Ce<sup>3+</sup>, β-sialon:Eu<sup>2+</sup>, Ca-α-sialon:Eu<sup>2+</sup>, and CaAlSiN<sub>3</sub>:Eu<sup>2+</sup> using NUV LED chip with a peak emission wavelength of 405 nm. The CRI and luminous efficacy of these white LEDs with CCTs of 2830–4350 K were \( \text{Ra} = 95–96 \) and 19–20 lm/W, respectively.

6. Summary

In this review, the crystal structures and luminescent properties of silicon-based oxynitride and nitride phosphors recently developed for use in white LEDs were described. The excited state of the 5d electrons of rare-earth elements is significantly lowered to low energies due to large crystal-field splitting and a strong nephelauxetic effect as a result of a high degree of crosslinking SiN<sub>4</sub> tetrahedra in the structure of silicon-based oxynitrides and nitrides. This enables silicon-based oxynitride and nitride phosphors to be excited efficiently by UV or blue-light irradiation, and then be applied as downconversion luminescent materials in white LEDs. The emission color of rare-earth ions (i.e., Eu<sup>2+</sup>, Ce<sup>3+</sup>, Yb<sup>2+</sup>) depends greatly on the surrounding environments including symmetry, coordination, covalence, bond length, site size, and crystal-field strength in which they reside, making it possible to adjust/tune the emission wavelength over a wide range by varying the compositional design. The novel class of oxynitride and nitride phosphors has demonstrated its superior suitability for use in white LED and can be used in bichromatic or multichromatic LEDs with excellent properties of high luminous efficacy, high chromatic stability, a wide range of white light with adjustable CCT, and brilliant color-rendering properties.

Acknowledgments

The studies described in this review were partially supported by Grants-in-Aid for the Encouragement of Young Scientists (B) Contract No. 17760550, from the Japan Society for the Promotion of Science (JSPS).

References

[1] S. Nakamura, G. Fasol, The Blue Laser Diode: GaN Based Light Emitters and Lasers, Springer, Berlin, 1997.
[2] U. Kaufmann, M. Kunzer, K. Kohler, H. Obloh, W. Pletschen, P. Schlotter, J. Wagner, A. Ellens, W. Rossner, M. Kobus, Phys. Stat. Sol. A 192 (2002) 246.
[3] J.K. Park, C.H. Kim, S.H. Park, H.D. Park, S.Y. Choi, Appl. Phys. Lett. 84 (2004) 1647.
[4] J.K. Park, K.J. Choi, J.H. Yeon, S.J. Lee, C.H. Kim, Appl. Phys. Lett. 88 (2006) 043511.
[5] D. Jia, D.N. Hunter, J. Appl. Phys. 100 (2006) 113125.
[6] Y.R. Do, K.Y. Ko, S.H. Na, Y.D. Huh, J. Electrochem. Soc. 153 (2006) H142.
[7] A.J. Steckl, R. Birkhahn, Appl. Phys. Lett. 73 (1998) 1700.
[8] A.A. Andreev, Phys. Solid State 45 (2003) 419.
[9] K.P. O'Donnell, B. Hourahine, Eur. Phys. J. Appl. Phys. 36 (2006) 91.
[10] A.J. Steckl, J.C. Heikennen, D.S. Lee, M.J. Garter, C.C. Baker, Y.Q. Wang, R. Jones, IEEE J. Sel. Topics Quantum Electron. 8 (2002) 749.
[11] N. Hirosaki, R.-J. Xie, K. Sakuma, Bull. Ceram. Soc. Jpn. 41 (2006) 602 (in Japanese).
[12] N. Hirosaki, R.-J. Xie, K. Sakuma, Oyo Buturi 74 (2005) 1449 (in Japanese).
[13] Y.Q. Li, H.T. Hintzen, Oyo Buturi 76 (2006) 258.
[14] R.-J. Xie, N. Hirosaki, M. Mitomo, in: W.Y. Yen, S. Shionoya, H. Yamamoto (Eds.), Phosphor Handbook, second ed, CRC Press, Boca Raton, 2007, p. 331.
[15] R. Marchand, Y. Laurent, J. Guyader, P. L'Haridon, P. Verdier, J. Eur. Ceram. Soc. 8 (1991) 197.
[16] H.A. Hoppe, H. Lutz, P. Morys, W. Schnick, A. Seilmeier, J. Phys. Chem. Solids 61 (2000) 2001.
[17] J.W.H. van Kreveld, H.T. Hintzen, R. Metselaar, A. Meijerink, J. Alloys Compd. 268 (1998) 272.
[18] J.W.H. van Kreveld, J.W.T. van Rutten, H. Mandal, H.T. Hintzen, R. Metselaar, J. Solid State Chem. 165 (2002) 19.
[19] R.-J. Xie, M. Mitomo, K. Uheeda, F.F. Xu, Y. Akimune, J. Am. Ceram. Soc. 85 (2002) 1229.
[20] K. Uheeda, H. Takizawa, T. Endo, H. Yamane, M. Shimada, C.M. Wang, M. Mitomo, J. Luminn. 87–88 (2000) 967.
[21] W. Schnick, H. Huppertz, Chem. Eur. J. 8 (1998) 679.
[22] W. Schnick, Int. J. Inorg. Mater. 3 (2001) 1267.
[23] H. Huppertz, W. Schnick, Chem. Eur. J. 3 (1997) 249.
[24] H. Huppertz, W. Schnick, Angew. Chem. Int. Ed. Engl. 35 (1996) 599.
[25] H. Huppertz, W. Schnick, Z. Anorg. Allg. Chem. 621 (1995) 1037.
[29] R.-J. Xie, N. Hirosaki, M. Mitomo, Y. Yamamoto, T. Suehiro, N. Ohashi, J. Am. Ceram. Soc. 87 (2004) 1368.
[30] R.-J. Xie, N. Hirosaki, M. Mitomo, T. Suehiro, X. Xin, H. Tanaka, J. Am. Ceram. Soc. 88 (2005) 2883.
[31] B. Dierre, R.-J. Xie, N. Hirosaki, T. Sekiguchi, J. Mater. Res. 22 (2007) 3242.
[32] N. Hirosaki, R.-J. Xie, K. Kimoto, T. Sekiguchi, Y. Yamamoto, T. Suehiro, M. Mitomo, Appl. Phys. Lett. 86 (2005) 211905.
[33] R.-J. Xie, N. Hirosaki, H.L. Li, Y.Q. Li, M. Mitomo, J. Electrochem. Soc. 154 (2007) 3314.
[34] R.-J. Xie, N. Hirosaki, M. Mitomo, K. Uheda, T. Suehiro, Y. Xu, Y. Yamamoto, T. Sekiguchi, J. Phys. Chem. B 109 (2005) 9490.
[35] Y.Q. Li, C.M. Fang, G. de With, H.T. Hintzen, Chem. Mater. 17 (2005) 3242.
[36] Y.Q. Li, A.C.A. Delsing, G. de With, H.T. Hintzen, J. Phys. Chem. B 109 (2005) 12027.
[37] R.-J. Xie, N. Hirosaki, K. Sakuma, Y. Yamamoto, M. Mitomo, Appl. Phys. Lett. 84 (2004) 5404.
[38] R.-J. Xie, N. Hirosaki, M. Mitomo, Y. Yamamoto, T. Suehiro, K. Sakuma, J. Phys. Chem. B 108 (2004) 12027.
[39] R.-J. Xie, N. Hirosaki, M. Mitomo, K. Takahashi, K. Sakuma, Appl. Phys. Lett. 88 (2006) 101104.
[40] R.-J. Xie, N. Hirosaki, M. Mitomo, K. Sakuma, N. Kimura, Appl. Phys. Lett. 89 (2006) 241103.
[41] Y.Q. Li, A.C.A. Delsing, G. de With, H.T. Hintzen, Solid State Chem. 177 (2004) 4687.
[42] R.-J. Xie, N. Hirosaki, K. Sakuma, Y. Yamamoto, M. Mitomo, Appl. Phys. Lett. 84 (2004) 4492.
[43] K. Uheda, N. Hirosaki, Y. Yamamoto, A. Naito, T. Nakajima, H. Yamamoto, Electrochem. Solid State Lett. 9 (2006) H22.
[44] R. Le Toquin, A.K. Cheetham, Chem. Phys. Lett. 423 (2006) 352.
[45] S.X. Zhang, T. Kono, A. Ito, T. Yasaka, H. Uchiike, J. Lumin. 106 (2004) 39.
[46] J. Grins, Z.-J. Shen, M. Nygen, T. Ekstrom, J. Mater. Chem. 5 (1995) 2001.
[47] S. Hampshire, H.K. Park, D.P. Thompson, K.H. Jack, Nature 274 (1978) 31.
[48] G.Z. Cao, R. Metselaar, Chem. Mater. 3 (1991) 242.
[49] T. Ekstrom, M. Nygen, J. Am. Ceram. Soc. 75 (1992) 259.
[50] F. Izumi, M. Mitomo, J. Mater. Sci. Lett. 1 (1982) 533.
[51] J. Grins, Z. Shen, S. Esmaeilzadeh, P. Berastegui, J. Mater. Chem. 11 (2001) 2358.
[52] Y. Oyama, O. Kamigaito, Jpn. J. Appl. Phys. 10 (1971) 1637.
[53] K.H. Jack, W.I. Wilson, Nat. Phys. Sci. 238 (1972) 28.