An investigation of crystal chemistry and luminescence properties of Eu-doped pure-nitride α–sialon fabricated by the alloy-nitridation method

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ABSTRACT

A novel synthesis route of Eu^{2+}-doped pure-nitride α-sialons has been reported. It is through an alloy-nitridation method at ~2173 K in nitrogen atmosphere, with stable alloys (CaAl, SiEu), AlN, and α-Si_3N_4 powders as starting materials. A linear relationship between the lattice parameters and m values of $(Ca_{0.995}Eu_{0.005})_{m/2}Si_{12-m}Al_mN_{16}$ compositions is obtained, indicating that our samples contain very little oxygen, i.e. herein so-called Eu-doped pure-nitride α-sialons. The $(Ca_{0.995}Eu_{0.005})_{m/2}Si_{12-m}Al_mN_{16}$ compounds with $2.4 \leq m \leq 4.0$ give the strongest emission. The emission shifts to longer wavelength with m values increasing as well as Eu contents increasing. $(Ca_{0.995}Eu_{0.005})_{m/2}Si_{12-m}Al_mN_{16}$ compositions with smaller m values exhibit better thermal quenching properties.

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1. Introduction

Eu^{2+}-doped α-sialons have attracted considerable interest in recent years owing to their potential application as down-conversion phosphors for white light-emitting diodes (LEDs), which combine excellent high temperature and chemical stability of α-sialons with the unique luminescence features of Eu^{2+} ions that exhibit parity-allowed, energy-efficient and broad 5d–4f absorption and emission [1–7]. The white LEDs will be new generation light sources with the advantages of energy-saving, long lifetime, compactness and environmental friendliness [8]. The white light can be generated by using a LED chip-phosphor system, in which the phosphor strongly absorbs ultraviolet (UV)–blue light (370–460 nm) from LED chip and efficiently re-emits in the red, green, or yellow part of the visible spectrum. Typical commercially available white LED features a combination of blue InGaN chips with $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce)-based phosphors [9–11]. However, this type of white light has a high correlated color temperature (CCT) and a poor color rendering index (CRI) because it lacks a red component, giving "cool"-white light. The need to fabricate "warm"-white LEDs with CCT of 2700–3200 K and high CRI greater than 80 has driven LED phosphor development toward novel compositions and structure types. Currently one important focus has been on Eu^{2+}/Ce^{3+}-doped silicon-based oxynitride and nitride phosphors whose emission can cover the entire visible spectrum due to the host lattice sensitivity of

Eu^{2+}/Ce^{3+} 4f–5d transitions in spectral positions [6]. Generally the energy of 4f–5d transitions can be lowered when Eu^{2+}/Ce^{3+} coordinates to less electronegative and higher formal charge nitrogen (N^{3-}) compared to oxygen (O^{2-}) due to the nephelauxetic effect (covalence) and the high ligand-field splitting of 5d level [12]. This reasoning has led to extensive studies on Eu^{2+}/Ce^{3+}-doped (oxy)nitride phosphors, including representative $M_2Si_5N_8$:Eu^{2+} (M=Ca, Sr and Ba) [13–18] and MAlSiN$_3$:Eu red phosphors [19–23], $MSi_2O_2N_2$:Eu^{2+} (M=Ca, Sr and Ba) [24–26] and $MYSi_4N_7$:Eu (M=Sr and Ba) green–yellow phosphors [27], and β/α-sialon:Eu green–yellow phosphors [1,2,28]. Sialons constitute an important family of materials with unique structural features and various crystal chemistries. The α-sialons are solid solutions of the M–Si–Al–O–N system, whose structure is derived from α-Si_3N_4, and can be represented as $M_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$, where m (Al–N) pairs and n (Al–O) pairs replace $m+n$ (Si–N) pairs in each unit cell, $x=m/v$, and v is valence of the M ion. M is a modifying cation, typically Li, Mg, Ca, Y or rare earth with $Z > 60$ [29]. In the α-sialon structure there are two interstitial sites per unit cell that can accommodate M cations; thus M content (x) is less than or equal to 2, and the values of m and x are taken to meet electroneutrality requirement, i.e. $x=m/v$. Because of their excellent mechanical properties and high temperature stability, α-sialon ceramics have been developed for structural engineering applications. Since the pioneering work of Krevel et al. [1] and Xie et al. [2] in 2002, the RE-doped α-sialon phosphors have received increasing attention. In particular Ca-α-sialon:Eu, which exhibits yellow emission (ca. 570–600 nm) and a strong absorption in the UV–blue spectral range (ca. 300–470 nm), has been proved to be a good down-conversion phosphor for white LED combined with a blue InGaN LED chip

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[3,4]. Generally, the Eu^{2+} ion alone cannot enter into and stabilize the α-sialon lattice due to its large ion size, but it does if codoped with Ca or Y [1]. However, recently Shioi et al. reported the synthesis and luminescence properties of Eu single-doped α-sialon prepared by solid-state reaction (SSR) [30].

The emission of Ca-α-sialon:Eu can be tuned by changing the composition, such as by changing the m and n values, by substituting Ca with other metals such as Li, Mg and Y, and by adjusting O, N content or Eu concentration [3,4,31–33]. Up to now, although α-sialon:Eu phosphors have been extensively investigated, there are few reports on low oxygen content (nitrogen-rich) Eu^{2+} doped Ca-α-sialon [33,34] and even fewer reports on pure nitride α-sialon [30], i.e. $M_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$ ($n=0$), or $M_xSi_{12-m}Al_mN_{16}$. According to the nephelauxetic effect argument in the development of LED phosphor, a pure nitride α-sialon host would further lower the energy of Eu^{2+} 5d level and shift emission to a longer wavelength region, meeting the requirements of warm white LED.

The pure nitride α-sialon contains no oxygen, and thus valence compensation is solely by the introduction of the modifying cations. Because there are only two sites per unit cell for these modifying cations, the upper limiting compositions for α-sialons with a v-valence metal ion are expected to be $M_2Si_{12-2v}Al_{2v}N_{16}$, e.g., $Ca_2Si_8Al_4N_{16}$. This upper limit has not been achieved, which may be due to the presence of oxygen in the silicon nitride particles [29]. The highest solubility has been reported to be 1.83 Ca^{2+} per cell in Ca-α-sialon with the composition $Ca_{1.83}Si_{8.34}Al_{3.66}N_{16}$. The upper limit of the solubility in Ca-α-sialon generally decreases as the size of the modifying cations becomes larger [35].

Oxygen-containing Ca-α-sialon:Eu^{2+} ($Ca_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$:$Eu^{2+}$ with much larger n values) phosphors have been extensively investigated due to the controllability of their compositions. In contrast, reports on pure-nitride Ca-α-sialon:Eu^{2+} ($Ca_{m/2}Si_{12-m}Al_mN_{16}$:$Eu^{2+}$) are very limited due to the fact that it is difficult to control the compositions. Recently, Piao et al. [34] reported synthesis and luminescence properties of low oxygen (≤ 0.7 wt%) content Ca-α-sialon:Eu^{2+} from cyanamide reduction, and Park et al [33]. prepared Eu^{2+} doped nitrogen-rich Ca-α-sialon. However, in these reports, with Eu_2O_3 as one of the starting materials, oxygen is inevitably incorporated into the α-sialon lattice. The investigation of Shioi et al. [30] suggests that the concentration of trivalent Eu^{3+}, which could be luminescent killer centers, linearly increases with the increase of oxygen content (i.e. n value). Therefore, the pure-nitride α-sialon:Eu (i.e. $Ca_{m/2}Si_{12-m}Al_mN_{16}$:$Eu^{2+}$, $n=0$) may give excellent photoluminescence properties, say, it may give longer wavelength emission vs. oxygen contained α-sialon:Eu due to the nephelauxetic effect. Furthermore, the perfect rigid framework of pure-nitride α-sialon:Eu may provide a crystal chemistry basis for good concentration quenching and thermal quenching properties.

In the past several years, some methods have been tried to synthesize the Eu^{2+}-doped sialon phosphors, such as solid-state reaction (SSR) at high temperature and high pressure [24], carbonthermal reduction nitridation (CRN) [36–39], gas reduction nitridation (GRN) methods [40,41], gas-pressured sintering (GPS) [42], and spark plasma sintering (SPS) [43]. To the best of our knowledge, the starting materials of all reported Eu-doped α-sialon synthesis methods involved oxides or seriously moisture sensitive materials; this limited the preparation and investigation of pure-nitride Eu-doped α-sialon. The SSR method has the advantages of improving luminescence efficiencies of phosphors and large-scale production. In this work, we have successfully synthesized Eu^{2+}-doped pure-nitride phosphors through SSR with stable alloys (CaAl and SiEu), AlN and α-Si_3N_4 as the starting materials, avoiding the oxygen incorporating into the α-sialon structure because of no oxides and seriously moisture sensitive

alkaline-earth and rare-earth nitrides (e.g. EuN and Ca_3N_2). Furthermore, we have investigated the structures and photoluminescence (PL) properties of the phosphors in detail.

2. Experimental

Two series of samples with different compositions were prepared: $(Ca_{0.995}Eu_{0.005})_{m/2}Si_{12-m}Al_mN_{16}$ with different Al/Si ratios (i.e. m values), and $Ca_{1.71-x}Si_{8.57}Al_{3.43}N_{16}$:$x$Eu with different Eu-doped concentrations (i.e. x values). The so-called pure-nitride α-sialon has the composition of $Ca_{m/2}Si_{12-m}Al_mN_{16}$ (called pure-nitride α-sialon hereafter), where the highest solubility of Ca is 1.83 (i.e. $m=3.66$), and the lowest solubility is zero (i.e. $m=0$), that is $Si_{12}N_{16}$ (Si_3N_4). In this work, we took a limit of m value, $0.375 \leq m/2 \leq 2.000$ (i.e. $0.750 \leq m \leq 4.000$), and prepared the samples with different nominal m values. In order to investigate the effects of Al/Si ratios on the crystal structures and luminescence properties, the Eu concentrations were kept at a very low level, i.e. not more than 0.5%, when $x=0.005$ and m values are within the above range.

According to the results of the first series of $(Ca_{0.995}Eu_{0.005})_{m/2}Si_{12-m}Al_mN_{16}$, when the m value is in the range of $3.0 \leq m \leq 4.0$, the Ca–α-sialon samples have excellent photoluminescence properties. This conclusion is also supported by the report of Sakuma et al. [31] Li et al. [41]. Thus, we have investigated samples of different concentrations Eu^{2+}-doped pure-nitride α-sialons with $m=3.43$ (Si/Al$=2.5$), i.e. the series $Ca_{1.71-x}Si_{8.57}Al_{3.43}N_{16}$:$x$Eu ($0 \leq x \leq 0.343$).

The starting materials included AlN (Hefei Kaier Nano, 99.5%) and Si_3N_4 (Hefei Kaier Nano, 99.5%) powders and CaAl, SiEu alloys, which were firstly prepared by argon arc melting of an appropriate amount of the metallic Ca, Al, Eu and Si (General Research Institute for Nonferrous Metal Beijing, 99.9%). To ensure the homogeneity of alloys the ingots were turned and melted several times. The purity of all starting materials was above 99.5% in quality proportion. With SiEu alloy as the dopant, different Eu concentrations (x values are 0.0086, 0.0171, 0.0514, 0.1029, 0.1371, 0.2057, 0.2571, and 0.3429) were adopted and the starting materials were stoichiometrically weighted according to the compositions. Then they were mixed and ground in an agate mortar with n-hexane as dispersant to avoid oxidation. When n-hexane dispersant volatilized completely, the solid mixtures were pressed into pellets and placed into a graphite furnace sequentially. The furnace chamber was pressurized to 0.3 MPa with a starting high-purity nitrogen atmosphere (99.99%) after being vacuumed to 10^{-3} Pa below. The samples were sintered at 2173 K for 4 h. After they had been furnace-cooled to room temperature, the as-prepared samples were crushed and ground into fine powder for further investigations of the photoluminescence properties and XRD analysis.

The emission and excitation spectra at room temperature were recorded on an Edinburgh FL920 fluorescence spectrophotometer with a Hamamatsu S900-R (red sensitive version) photomultiplier tube (PMT). The spectra resolution was 1.0 nm. The monochromators slits for both excitation and emission were kept at 0.3 nm, and dwell period at each wavelength (Dwell Time) was 0.20 s. The wavelength scan speed was 200 nm min^{-1}. The spectral scan range covered at least 450–700 nm. The same instrumental settings were applied in all measurements for comparison. The emission and excitation spectra at low temperature were tested on FL920 fluorescence spectrometers manufactured by Edinburgh Instruments Ltd. Corporation. The spectral scan maximum extended to 800 nm, and the scan step was 0.1 nm. Using a closed loop liquid helium refrigeration system, we acquired the spectra at low temperature through cooling of the samples to 10–350 K.