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# Luminescent properties and microstructure of SiC doped AlON: Eu<sup>2+</sup> phosphors



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# A R T I C L E I N F O

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# ABSTRACT

Superior thermal quenching and degradation of phosphors are required for long lifetime lighting devices, such as light-emitting diodes, which can be realized through composition modification. Here, Al-N bonds in AlON:  $Eu^{2+}$  phosphors are substituted by higher bond order of Si-C. Photoluminescence (PL) results show thermal quenching (at 150 °C) and thermal degradation (after 600 °C treatment in air) are improved by 5% and 8% with a small decrease of PL intensity in 5% SiC doped AlON:  $Eu^{2+}$  phosphor. To explain these observations, first-principles computational study was performed to understand the Si and C configuration in AlON: $Eu^{2+}$ . The calculations reveal that Si and C elements are not randomly distributed in AlON lattice. It was found that Si prefers occupying tetrahedral sites (Td-Si) and the insertion of C in Td-Si is always energetically favorable, which results in the formation of SiC<sub>4</sub> and SiNC<sub>3</sub> clusters. Thus, the Al-N substitution by Si-C induces a stronger local structure, which accounts for the emission redshift and better thermal stability.

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# 1. Introduction

As one of the crucial components for phosphor-converted white light-emitting diodes (LEDs), environmental-friendly, high-efficiency and good stability phosphors are required in order to meet our energy demands [1,2]. Generally, white emission can be generated by the combination of blue LED chip with yellow phosphor such as YAG: Ce<sup>3+</sup> or of ultraviolet LED chip with blue, green and red phosphors. Accordingly, the discovery and performance improvement of phosphors are of great importance in order to produce highly efficient and reliable lighting devices.

Rare-earth-doped nitride and oxynitride phosphors have

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attracted much considerable attention, due to their outstanding performances including superior thermal stability, proper excitation range from ultraviolet (UV) to blue light and adjustable emission wavelength through tuning the composition stoichiometry of phosphors [3–10]. These excellent photoluminescence properties make them appropriate phosphors for white LEDs.

 $\gamma$ -Aluminum oxynitride with spinel structure (hereafter AlON) is well known as a transparent ceramic in the visible light range and it has superior mechanical properties both at room and high temperatures [11]. As a spinel compound, which demands totally 32 anions and 24 cations per unit cell (Mg<sub>8</sub>A1<sub>16</sub>O<sub>32</sub>, i.e., MgA1<sub>2</sub>O<sub>4</sub>), AlON can be described by the following formula: Al<sub>(64+z)/3</sub>V<sub>(8-z)/3</sub>O<sub>32-z</sub>N<sub>z</sub>, where V is cation vacancy as proposed by McCauley [12]. Basically, in the AlON spinel unit cell, there are 23 Al cations in tetrahedral and octahedral sites at most and 1 Al vacancy (V<sub>Al</sub>) forming the composition of Al<sub>23</sub>O<sub>27</sub>N<sub>5</sub> (N = 5). Octahedrons are connected to each other by edge sharing and to the tetrahedrons by

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point sharing. The Al vacancy is prone to stay in the octahedral sites in AlON structure based on the calculation results of density functional theory (DFT) [13,14]. Simultaneously, AlON has been evaluated as a promising host-lattice for transition or rare-earth ions doping [15–18]. In particular, when doped with Eu<sup>2+</sup> ions, AlON can be developed into an interesting blue-green luminescent material which exhibits a strong emission band centered at 480–500 nm under UV light irradiation [19–21].

For practical use, thermal stability of phosphors is an important factor that strongly affects the lifetime, efficiency and color rendering of the luminescent devices. Actually, there are two main different aspects associated with the thermal stability: thermal quenching and thermal degradation. Thermal quenching behavior, which is related to a reversible decrease of the luminescence intensity with temperature increase, typically in the temperature range of 25-300 °C, is commonly observed in phosphors and intrinsic property of the material, which cannot be easily avoided. An gradually accepted model for thermal quenching is the thermal ionization of the 5d electron to the conduction band of the host lattice [22]. On the contrary, thermal degradation is an irreversible change in the luminescence properties, which is generally caused by the oxidation of luminescent ions (i.e.,  $Eu^{2+}$  to  $Eu^{3+}$  and  $Ce^{3+}$  to  $Ce^{4+}$ ) at high temperature (300–600 °C). To overcome the latter problem, a very thin metal oxide layer is coated on the surface of the phosphors to isolate the phosphors against the attack from O<sub>2</sub>, which consequently alleviates the degradation [23–25].

Here, we demonstrate an approach to improve the thermal quenching and thermal degradation of  $Eu^{2+}$  doped AlON phosphors via composition modification. Due to the similarities of neutral charges and bong lengths between Al-N and Si-C, it is expected that AlON will keep its charge balance and crystal structure upon the substitution while its increased covalency and crystal rigidity is supposed to improve its thermal stability. We find that both thermal quenching and thermal degradation are improved in SiC-doped AlON: Eu<sup>2+</sup> phosphor. This improvement may be correlated to the structural modifications induced by SiC doping. Indeed, an intriguing aggregation of SiC<sub>4</sub> and SiNC<sub>3</sub> is observed through NMR results. First-principles computational study reveals that the insertion of C to tetrahedral Si is always energetically favorable, whereas for octahedral Si it is energetically allowed but impossible to accommodate more C due to C2 dimer formation.

# 2. Experimental section

# 2.1. Material synthesis

As a host-lattice material. AlON showed the stoichiometry of Al<sub>23</sub>O<sub>27</sub>N<sub>5</sub>, i.e. 9Al<sub>2</sub>O<sub>3</sub>-5AlN. By replacing AlN by SiC, the formula became 9Al<sub>2</sub>O<sub>3</sub>-5(1-x)AlN-5xSiC. Fixed 0.2mol% Eu and 10mol% Mg compared to total cation number were introduced to give the luminescence properties and promote the high purity of AlON, respectively. For simplicity, the overall starting compositions were written as AlON:Eu, xSi-C, where x represents the mole fraction of SiC substitution for AlN. The powder mixtures of Al<sub>2</sub>O<sub>3</sub> (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), AlN (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), MgO (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), β-SiC (Aladdin Co. Ltd, Shanghai, China) and Eu<sub>2</sub>O<sub>3</sub> (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) were hand-grinded sufficiently in a Si<sub>3</sub>N<sub>4</sub> mortar. The obtained mixtures were fired by solid-state reaction in BN crucibles under N<sub>2</sub> atmosphere for 20 h at 1800 °C with a heating rate of 420 °C/h and cooled down naturally.

#### 2.2. Material characterization

The phase formation was analyzed by an X-ray diffractometer (Model PW 1700, Philips Research Laboratories, Eindhoven, the Netherlands) using Cu K<sub> $\alpha$ </sub> radiation at a scanning rate of 0.5°/min. The microstructure was analyzed by transmission electron microscopy (Model 2100F, JEOL, Tokyo, Japan). The solid state nuclear magnetic resonance (NMR) spectra were recorded on a 14.1-T widebore Bruker Avance III-400 spectrometer. The Larmor frequency was 119.2 MHz and pulse width was set as 2.5 µs. Metallic elements content was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES) (Optima 7300DV, Perkin Elmer Corporation, USA). The amount of carbon was determined by high frequency infrared carbon-sulfur analyzer (EA-CSA-05, U-THERM INTERNATIONAL (H.K.) Ltd, China).

## 2.3. Computational methodology

The CASTEP code is used to perform calculations in the present work [26], which is based on DFT and uses planewave to expand wavefunctions and densities, and pseudopotenial to treat the interaction between valence electron and ionic core [27].

In this work we use PBE GGA-PBE exchange correlation functional. Norm-conserving pseudopotential was generated by OPIUM code [28–30]. Test of these pseudopotentials indicates the typical error to be within 2% in lattice parameter compared with experimental data from crystal structure database. A kinetic energy cutoff of 780 eV was used, which results in convergence of total energy with respect to cut-off energy being smaller than 0.1 eV per atom. Actual spacing of k-point sampling is 0.065 Ang<sup>-1</sup>.

Accuracy test comparing calculated undoped structure with measured values indicates that the lattice parameter error is -2.3%, however, pseudopotentials of Al, Si, O, N and C used in this work at same E\_cut quality, yielding lattice parameter errors (when compared with experimental values) Err (a = b = c) = -2.75% for  $Al_2O_3$  with primitive cell, Err(a = b, c) = (-1.13%, 0.58%) for AlN, E(a = b, c) = (0.54%, 0.59%) for  $\alpha$ -SiO<sub>2</sub> and Err (a = b) = (0.69\%, c) 0.90%) for SiC, respectively. The smaller lattice parameter for Al containing materials (Al<sub>2</sub>O<sub>3</sub> and AlN) can be attributed to a bigger core Al norm-conserving pseudopotential. When Al is replaced by an ultrasoft Al [31], the errors become Err (a = b = c) = 0.58% for  $Al_2O_3$  and Err (a = b, c) = (0.44%, 0.55%) for AlN. As for AlON, we achieved to have Err (a = c) = 0.60% and Err (b) = 0.66%. This favorable all-round agreement gives us confidence on the follow up calculations. All pseudopotentials used in the present work can be found in CASTEP Pseudopotential Library in Materials Studio version 5.5 and the later.

#### 2.4. Luminescence properties

The photoluminescence spectra from 180 K to room temperature were monitored by a fluorescent spectrophotometer (Model FLUOROLOG-3-TAU, Jobin Yvon, France) equipped with a liquid N<sub>2</sub> cryostat (Model CCS-355, Janis, USA). The temperature dependent luminescent spectra from room temperature to 573 K were measured by a fluorescent spectrophotometer (Model F-4600, Hitachi, Tokyo, Japan) equipped with a high temperature fluorescence controller (Model TAP-02, KOJI instrument Co. Ltd, Tianjin, China). The emission intensity at room temperature is fixed at the value determined with the other fluorescent spectrophotometers with the intention to combine spectra at low and high temperature together. The emission spectrum from F-4600 was corrected for the spectral response of the monochromator and Hamamatsu R928P photomultiplier tube (Hamamatsu Photonics K.K., Hamamatsu, Japan) by a light diffuser and tungsten lamp (Noma Electric Corp., NY; 10V, 4A). The excitation spectrum was also corrected for the spectral distribution of the xenon lamp intensity by measuring rhodamine-B as a reference. Diffuse-reflectance spectra were measured at room temperature by a UV–Vis–NIR spectrophotometer (Model CARY 5000, Agilent Technologies, USA) equipped with an integrating sphere (Model Internal DRA-2500, Agilent Technologies, USA).

# 3. Results and discussion

# 3.1. Material properties

Phase purity and lattice parameters of AlON: Eu, xSi-C samples were investigated by using XRD. Both AlN and SiC belong to the same hexagonal structure with the space group *P*63*mc*. The bond length of Al–N in AlN and Si–C in SiC is ~1.885 and ~1.880 Å, respectively. This enables AlN and SiC to form a solid solution in a small range of composition. As a result, SiC can partly replace AlN and reacts with Al<sub>2</sub>O<sub>3</sub> and AlN to form a spinel structure with a composition of 9Al<sub>2</sub>O<sub>3</sub>-5(1-x)AlN-5xSiC. As seen in Fig. 1(a), a pure phase of AlON can be achieved when x is below 10%. Above further increasing of x, some secondary phases, such as EuAl<sub>12</sub>O<sub>19</sub>, appear [21], indicating the solubility of SiC in AlON is less than 10%. It should be noted that this value is remarkably smaller than the solubility of SiC (40%) in Al<sub>1-x</sub>Si<sub>x</sub>C<sub>x</sub>N<sub>1-x</sub>:Eu<sup>2+</sup>phosphor [32].

In addition, the XRD peaks progressively shifted to larger angles owing to the smaller Si<sup>4+</sup> ( $^{IV}r(Si^{4+}) = 0.26$  Å) substitution for the larger isoelectronic species Al<sup>3+</sup>( $^{IV}r(Al^{3+}) = 0.39$  Å) in AlON lattice

[33]. The calculated lattice parameters based on XRD peak position are shown in Fig. 1(b), evidencing the minor lattice shrinkage of AlON with the increase of SiC substitution. Through careful investigation on the relative XRD intensity, the peak intensity at 37.5° related to (3 1 1) plane gradually decreases, whereas the peak at 66.5° related to (4 4 0) plane increases, as seen in Fig. 1(c). This phenomenon is associated with the structure change caused by SiC doping, which will be discussed later.

The part elemental composition Eu: Mg: Al: Si: C ratio of AlON: Eu, xSi-C (x = 10%), i.e. Eu<sub>0.048</sub>Mg<sub>2.38</sub>Al<sub>21.38</sub>Si<sub>0.5</sub>O<sub>27</sub>N<sub>4.5</sub>C<sub>0.5</sub> is 0.048: 1.93: 23.41: 0.46: 0.31. The Mg and C content is relatively low, indicating the volatility of Mg and oxidation of C in the preparation process.

Fig. 2 gives the elemental mapping of AlON: Eu, xSi-C (x = 5%). It confirms that the crystal particle is composed of Al, O, N, Mg, Si, C and minor Eu. All element mappings are in accordance with the TEM images of the particle shapes. EDS mapping result shows the uniform distribution of Si and C elements in AlON particle, validating the dissolution of SiC into AlON lattice. Although the signal corresponding to Eu is quite weak due to its low concentration, it is still clear to see that the Eu distribution matches the particle shape. This indicates that the Eu is dissolved into AlON lattice.

Unfortunately, the exact sites of  $Eu^{2+}$  ions in AlON lattice have not yet been reported since it is a challenging work to make it clear. On account of large difference of ionic radius between  $Eu^{2+}$  and  $Al^{3+}$ ,  $Eu^{2+}$  ions are expected to locate at some layered structure, which has been verified in Eu, Si co-doped AlN [34]. Ascribed to the presence of rare-earth element and  $Al_2O_3$  in the synthesis of AlON:



**Fig. 1.** (a) XRD patterns of AlON: Eu, xSi–C samples. The arrows indicate the second phase formed in the product when x is 10%; (b) lattice parameters of AlON: Eu, xSi–C samples. The error bar is shown in red; (c) the ratio of XRD intensity at 37.5 and 66.5°. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. EDS elemental mapping of AlON: Eu, xSi-C (x = 5%) sample, showing the elements distribution in AlON particle.

Eu phosphors, It is possible to form a new superlattice consisting of the beta alumina or magnetoplumbite structures inside the AlON crystal lattice, which are representative for  $BaMgAl_{10}O_{17}$  and  $SrAl_{12}O_{19}$ , respectively [35]. Some progress has been achieved in observing the abnormal structure and Eu sites in AlON lattice. However, we have to admit that more time and patience are required to clarify this tough work, which will be discussed in future research.

Solid state NMR spectroscopy provides a description of local arrangement of central ions. The  $^{29}$ Si NMR spectrum is shown for qualitative studies of local Si sites. As shown in Fig. 2, three obvious chemical shifts at -12.6, -19.4 and -70 ppm are seen for the compositions of x = 2% and x = 10%, which can be assigned to SiC<sub>3</sub>N, SiC<sub>4</sub> and SiCO<sub>3</sub>, respectively [36–38]. These results indicate Al–N bond is partially substituted by Si–C bond and Si is prone to stay in the tetrahedral site forming Si(C, N, O)<sub>4</sub> coordination instead of octahedral site. The significantly strong peaks of  $SiC_3N$  and  $SiC_4$ show that Si is easily bounded to C but not to N or O solely in AlON lattice. This means that SiC doping forms local cluster and there is a preferred configuration for Si-C occupation. From the view of charge balance, C occupation site should be close to Si in order to achieve local charge balance. The same kind of local charge compensation through forming cluster can also be found in  $Al_{1-}$  $_xSi_xC_xN_{1-x}$ : Eu<sup>2+</sup> and (CaMg)<sub>x</sub>(NaSc)<sub>1-x</sub>Si<sub>2</sub>O<sub>6</sub> solid solutions [32,39]. Therefore, the change of  $I_{37,5}^{\circ}/I_{66,5}^{\circ}$  in XRD patterns is possibly caused by the preferred configuration for Si–C occupation in AlON lattice.

Nanostructures of three AlON: Eu, xSi–C samples are investigated using HRTEM as shown in Fig. 4 (a). Typical HRTEM images of the x = 0 sample show a very uniform contrast, indicating that these single-phase particles are highly crystalline without significant defects. However, micrographs of the x = 5% and 10% samples reveal obvious stacking faults structure. In the corresponding Fast Fourier Transform images (FFT), it can be seen that there is streaking of reflection spots caused by the stacking faults [40]. Owing to the smaller ions radius and high charge of Si<sup>4+</sup> against Al<sup>3+</sup>, it will attract the coordinated anions and be bonded to O<sup>2-</sup>, N<sup>3-</sup> or C<sup>4-</sup> strongly according to the Coulomb's law. From the NMR results in Fig. 3, Si and C are bonded together and consequently this Si(C, N, O)<sub>4</sub> tetrahedron will deform. Therefore, the observed stacking faults should be the domain region where Si–C substitutes Al–N bond in AlON lattice, as shown in the schematic diagram of Fig. 4(b).

During deformation, atoms can be pushed out of their place. If this happens to produce a symmetrical arrangement, it produces deformation twins. The sample with composition x = 10% shows a twinned structure, as the blue arrows indicate in Fig. 4 (a). The adjacent twins result in twisted domains and produce annular arranged reflections in FFT in Fig. 4. These significant observations identify the induced structure changes by SiC doping, which should be ascribed to the local cluster of SiC doping.

Taken the central ions  $Si^{4+}$  into consideration,  $Si^{4+}$  cations are coordinated by first-neighbor anions ( $C^{4-}$ ,  $N^{3-}$  or  $O^{2-}$ ) through linking of coordination polyhedra, as shown in Fig. 4 (c). As x increases, more Si is bounded to C and forms tetrahedral Si(C, N, O)<sub>4</sub>. Thus, the SiC/AlN substitution has a strong effect on bonding strength of O–Si. The degree of covalency in the O–Si bonding is competed by the stronger bonding of C–Si. The bonding strength of



**Fig. 3.** <sup>29</sup>Si NMR spectroscopy in AlON: Eu, xSi-C samples with x = 0.02 and 0.10.



**Fig. 4.** (a) High resolution TEM of AlON: Eu, xSi–C samples with x = 0, x = 5% and x = 10%. The inset is the corresponding Fast Fourier transform images (FFT); (b) a schematic diagram to show the stalking faults induced by SiC doping; (c) a schematic diagram to show the change of bond order and explain the reason why the second phase EuAl<sub>12</sub>O<sub>19</sub> is easily formed after SiC doping.

O–Si becomes less as the Al–N are replaced by Si–C with increasing x. Eu can easily react with the O atoms forming secondary phase EuAl<sub>12</sub>O<sub>19</sub>. This explain why the solubility of SiC in AlON: Eu, xSi–C is smaller than that in  $Al_{1-x}Si_xC_xN_{1-x}$ :Eu<sup>2+</sup>phosphor.

Fig. 5 (a) shows the diffuse reflection spectra of AlON: Eu, xSi–C performed at room temperature. The spectra show similar characteristic in the range of 250–800 nm. These phosphors have absorption bands in the UV region situated at ~265 and 360 nm. Undoubtedly, the second band is caused by the absorption of Eu<sup>2+</sup>. Considering that spinel  $Al_{23}O_{27}N_5$  is calculated to have a wide band gap around 5 eV [41], the first absorption band is probably ascribed to the host lattice.

Due to the lattice shrinkage and larger electronegativity of  $C^{4-}$  than  $N^{3-}$ , it is speculated that  $Eu^{2+}$  will suffer from stronger crystal field and nephelauxetic effect, which results in an excitation and emission redshift in AlON: Eu, xSi–C samples. As shown in the PL spectra measured at room temperature (Fig. 5 (b)), both excitation and emission spectra show a substantial red-shift as x increases from 0 to 10%. On the other hand, Si–C doping shows the disadvantages that the emission intensity systematically decreases. It can be explained by the formation of defects caused by Si-C doping in the crystal lattice of AlON: Eu, xSi–C, which can work as luminescence guenching centers and decrease the emission intensity.

As seen in Fig. 5 (b), the emission peak is located at 470-490 nm with varying SiC contents. This is quite different from the EuAl<sub>12</sub>O<sub>19</sub>

and EuAl<sub>11</sub>O<sub>16</sub>N sample, whose emission peak covers 400–410 nm [35]. EuMgAl<sub>10</sub>O<sub>17</sub> normally shows excitation peak at 345 and 385 nm, and emission peak at 480 nm [35], which seems close to present PL results: excitation peak at 330 and 380 nm and emission peak at 480 nm. It is deduced that Eu forms layered structure resembling to EuMgAl<sub>10</sub>O<sub>17</sub> in the AlON lattice. Compared to EuMgAl<sub>10</sub>O<sub>17</sub>, AlON: Eu, xSi–C phosphors show much broader excitation and emission band, implying that the real structure around Eu have lower symmetry. The reason for this is possibly because the incorporated N or C are coordinated with Eu ions.

Thermal stability is a significant factor for phosphors in practical use. The progressive replacement of  $Al^{3+}$  and  $N^{3-}$  by  $Si^{4+}$  and  $C^{4-}$  is expected to introduce more covalency into the materials and hence raise lattice rigidity and the quenching barrier height. Fig. 6(a) shows the temperature-dependent emission intensity of AlON: Eu, xSi-C phosphors from 180 to 573 K. The thermal quenching is improved due to Si-C substitutions for Al-N bond. For instance, at a general working temperature for white LEDs (150 °C), the emission intensity of the phosphors with composition (x = 0) and (x = 5%) maintains 71% and 79% versus the emission intensity at 180 K, respectively. In addition, thermal degradation is also improved to same extent by Si-C doping. As shown in Fig. 6 (b), the emission intensity of AlON: Eu<sup>2+</sup> phosphor decreases 48% after annealing at 600 °C for 2 h in air, while that of AlON: Eu, xSi-C (x = 5%) decreases 40%. The degradation is caused by the oxidation of Eu<sup>2+</sup> into Eu<sup>3+</sup> in air [42,43,44]. Si–C doping helps form more



**Fig. 5.** (a) Diffuse reflection spectra of AlON: Eu, xSi–C performed at room temperature; (b) Excitation ( $\lambda_{em} = 480 \text{ nm}$ ) and emission spectra ( $\lambda_{ex} = 330 \text{ nm}$ ) in AlON: Eu, xSi–C samples.

rigid (Si, Al)–(C, O, N) network, which prevents oxygen attack and the oxidation of  $Eu^{2+}$  to  $Eu^{3+}$  [45]. Moreover, the emission clearly shifts to higher wavelength after annealing for x = 0%, while not for x = 5%.

Based on the above results, it seems interesting that Si is prone to get bounded to C and forms  $Si(C, N, O)_4$  tetrahedron in SiC doped AlON lattice. Because of the big effect of crystal structure on the luminescence properties, it is worthy clarifying the Si-C configuration in AlON lattice. Unfortunately, it is difficult to achieve valuable information on the Si–C segregation directly using experimental observation. High-angle annular dark-field (HAADF) STEM, which is capable of atomic-scale resolution and provides contrast based on the Z number, is not available in present work on account of the close Z number ( $Z_{AI} = 27$ ,  $Z_{Si} = 28$ ;  $Z_O = 16$ ,  $Z_N = 14$ ,  $Z_C = 12$ ). Instead, first-principle calculation is a strong compensation to investigate the minor structure change before and after Si-C doping.

# 3.2. Theoretical calculation

So far, there have been many researches investigating the crystal structure of single AlON phase with the ideal composition of  $Al_{23}O_{27}N_5$  [13,14,46]. It is concluded that the optimal AlON structure shows the following characteristics: (1) Aluminum vacancy is located at the octahedral sites with only oxygen as nearest neighbors; (2) Nitrogen atoms distribute far away from each other. Therefore, we can use the widely accepted AlON model with composition of  $Al_{23}O_{27}N_5$  as a starting point as shown in Fig. 7. All the followed Si<sub>Al</sub> or C<sub>N/O</sub> substituted structures are based on the preliminary  $Al_{23}O_{27}N_5$  structure [13]. There are mainly four issues in this calculation part. 1). why does Si prefer to occupy tetrahedral site? 2). why do Si and C prefer to be bonded to each other? 3). why can additional insertion of C form a bonded Si–C<sub>n</sub> or Si–NC<sub>n</sub> ( $n \ge 3$ ) 4). what happens to the structural properties in the SiC doped AlON?

# 1) Substitutional Si<sub>Al</sub>

The preference of Si site occupation needs to be determined firstly. Four tetrahedral Si(O,N)<sub>4</sub> and three octahedral Si(O,N)<sub>6</sub> configurations are proposed in the Si doped AlON, as shown in Fig. 7. We perform calculations to compare total energies of AlON with various Si<sub>Al</sub> defect sites. As shown in Table 1, with neutral valence charge and +1 valence charge, the latter is iso-electronic to the host crystal. The actual change state of the system depends on the chemical potential, which is controlled by the synthesis process such as excess charge at grain boundary or surface morphology. The result shows that in a reasonable charge state range, Td–Si–O<sub>3</sub>N and Oh–Si–O<sub>4</sub>N<sub>2</sub> are energetically most favorable.

## 2) Neutral substitution of Al and N pairs by Si and C

When one Si atom and one C atom replace one Al atom and one N atom in the AlON cell (Si<sub>Al</sub> and  $C_N$ ), the unit cell remains neutral.



Fig. 6. (a) Thermal quenching of AlON: Eu, xSi-C phosphors from 180 to 573K; (b) Thermal degradation of AlON: Eu, xSi-C phosphors after annealing at 600 °C for 2 h in air.



**Fig. 7.** Structural model of  $Al_{23}O_{27}N_5$  (AION), tetrahedral Si<sub>Al</sub> substitution in corner (Td-Si- $O_3N_c$ nr), quasi-face-center (Td-Si- $O_3N_q$ fc), Td-Si- $O_3N_q$ quater (Td-Si- $O_3N_q$ tr), Td-Si- $O_4$  and octahedral Si<sub>Al</sub> substitution Oh-Si- $O_4N_2$ , Oh-Si- $O_5N$ , Oh-Si- $O_6$ , respectively.

## Table 1

Relative total energies of AlON and volume change with various Si<sub>Al</sub> sites. For neutral cell, Td–Si–O<sub>3</sub>N\_cnr (used as reference) and Oh–Si–O<sub>4</sub>N<sub>2</sub> have lowest energy, indicating that these are two most preferable sites. For +1 charge state of cell, the order basically remain the same, except that lowest energy site shifts to Td–Si–O<sub>3</sub>N\_qrc from Td–Si–O<sub>3</sub>N\_cnr Td–Si site but both are still very close. Relative volume difference with respect to host cell is indicated in the parentheses. One can see volume correlate nicely to the relative energy for the case of neutral cell, but less so in the case for +1 charge cell.

Configuration	ΔE (eV)	Volume change
Neutral valence charge		
Td-Si-O <sub>4</sub>	0.85448208	0.65%
Td-Si-O <sub>3</sub> N_qtr	0.35211572	0.58%
Td-Si-O <sub>3</sub> N_qfc	0.31334978	0.29%
Td-Si-O <sub>3</sub> N_cnr	0.00000000	0.07%
Oh-Si-O <sub>4</sub> N <sub>2</sub>	0.01010694	0.67%
Oh–Si–O <sub>5</sub> N	0.43109018	0.47%
Oh–Si–O <sub>6</sub>	1.04715138	0.89%
+1 valence charge		
Td–Si–O <sub>4</sub>	1.45354692	-2.11%
Td–Si–O <sub>3</sub> N_qtr	0.39732195	-2.52%
Td-Si-O <sub>3</sub> N_qfc	-0.01388716	-2.51%
Td-Si-O <sub>3</sub> N_cnr	0.00000000	-2.48%
Oh-Si-O <sub>4</sub> N <sub>2</sub>	0.26679550	-2.43%
Oh–Si–O <sub>5</sub> N	0.75928952	-2.32%
Oh–Si–O <sub>6</sub>	1.12049522	-2.20%

This is an efficient way to maintain charge neutrality of doped system at wide range of doping concentration. We compared cases where  $Si_{Al}$  and  $C_N$  sites to be closely bonded together or separate. The configuration for bonded or separated Si–C pair after structure relaxing is shown in supporting information (Fig. S1). It turns out that bonded configuration has a lower total energy (0.49 eV). Strong covalent double bond between Si and C, as can be seen from Mulliken population analysis, as shown in Table 2, is the main reason for this preference.

As discussed above, the degree of covalency in the O–Si bond is competed by the double bonded C–Si. From Table 2, it is noted that

the bond order of O–Si decreases from 0.63 to 0.58 when C and Si is bonded, indicating O–Si bond becomes less rigid and easier to break. In that way, Eu can easily attack the O atoms and form secondary phase of EuAl<sub>12</sub>O<sub>19</sub> (in Fig. 1 a), resulting in low experimental Si–C doping limitation.

We also investigated the possibility of exchanging ions in the bonded Si–C pair in their Al and N sites, by switching the position of Si and C, and we found that the energy always significantly increases (typically 6 eV per Si–C pair), namely Si prefers Al sites. This behavior of Si is consistent with the element's general chemical characteristic bonding in aluminum silicate that Si and Al are easily interchangeable.

Table 2

Bond order and bond length comparison of a Si-C pair in bonded or separated configuration. Bond order and bond length between Si, C and their nearest neighbor are shown. Note that the double bond (bond index 1.16) is formed between Si and C when bonded, which accounts for the lower of total energy than separated case.

atom-pairs	bond order	bond length (Å)
Si—C (far apart)		
O(1)–Si	0.63	1.65136
N—Si	0.82	1.70963
O(2)-Si	0.54	1.71522
O(3)-Si	0.54	1.71522
C-Al(1)	0.97	1.85203
C-Al(2)	0.72	1.92083
C-Al(3)	0.72	1.92083
C-Al(4)	0.63	1.93042
Si-C (bonded)		
O(1)-Si	0.58	1.67104
C—Si	1.16	1.71671
O(2)-Si	0.46	1.77372
O(3)-Si	0.46	1.77372
C-Al(1)	0.61	1.91602
C-Al(2)	0.61	1.91602
C–Al(3)	0.53	1.91822

#### Table 3

Total energy difference (in eV) after the insertion of one carbon atom into an existing Td–Si cluster forming Si–C<sub>x</sub> or Si–NC<sub>x</sub> cluster starting from Td–Si–O<sub>3</sub>N\_cnr. These cases are all referring to 4-fold bonded cluster of Si, the number of oxygen is trivial and is therefore not assigned into the notation for clarity.

Starting from Td−Si−O <sub>3</sub> N_cnr	
Configuration (Si–C <sub>x</sub> )	$\Delta E (eV)$
$Si-O_3N + C \rightarrow Si-O_3C$	-0.487
$Si-O_3C + C \rightarrow Si-O_2C_2$	-0.652
$Si-O_2C_2 + C \rightarrow Si-OC_3$	-0.325
$Si-OC_3 + C \rightarrow SiC_4$	-0.055
Starting from Td–Si–O <sub>3</sub> N_cnr	
Configuration (Si-NC <sub>x</sub> O <sub>3-x</sub> )	$\Delta E (eV)$
$Si-O_3N + C \rightarrow Si-O_2NC$	-0.277
$Si-O_2NC + C \rightarrow Si-ONC_2$	-0.633
$Si-ONC_2 + C \rightarrow Si-NC_3$	-2.181

#### Table 4

Relative energies (in eV) of a C atom inserted into an existing 6-fold site forming  $Si-N_{2-y}C_{x+y}O_{4-x}$  (C replaces N and O) or  $Si-N_2C_xO_{4-x}$  (C replaces O) cluster starting from Oh–Si– $O_4N_2$ . x and y represent the amount of C substitution for O and N, respectively.

Starting from Oh–Si–O <sub>4</sub> N <sub>2</sub> .	
Configuration (Si $-N_{2-y}C_{x+y}O_{4-x}$ )	$\Delta E (eV)$
$Si-O_4N_2 + C \rightarrow Si-O_4NC + N$	-1.050
$Si-O_4NC + C \rightarrow Si-O_3NC_2 + O$	-0.277
$Si-O_3NC_2 + C \rightarrow Si-O_2NC_3 + O$	0.301
$Si-O_2NC_3 + C \rightarrow Si-O_2NC_4 + O$	-0.886
Starting from Oh–Si–O <sub>4</sub> N <sub>2</sub>	
Configuration $(Si-N_2C_xO_{4-x})$	$\Delta E (eV)$
$Si-O_4N_2 + C \rightarrow Si-O_3N_2C + O$	-0.445
$Si-O_3N_2C + C \rightarrow Si-O_2N_2C_2 + O$	-0.817
$Si-O_2N_2C_2 + C \rightarrow Si-ON_2C_3 + O$	-0.549
$Si{-}ON_2C_3+C \rightarrow Si{-}N_2C_4+O$	-1.287

3) Additional insertion of C atom forming a bonded Si $-C_n$  or Si $-NC_n$  clusters in Td and Oh sites

As mentioned previously, defect energy of Si occupying at corner-Td $-O_3N$  and Oh $-O_4N_2$  are very close, so in thermodynamically speaking, both 4-fold and 6-fold coordinated Si defects are equally possible. To explain why only tetrahedral Si-C<sub>4</sub> and Si-NC<sub>3</sub> are observed experimentally, rather than octahedral ones, we investigate whether subsequent carbon already comes inside the cell and becomes a stable defect, such as C<sub>N</sub> or C<sub>0</sub>, which can be

bonded to an existing tetrahedral and octahedral Si defect cluster. Firstly, C insertion into tetrahedral Si site is considered. From Table 3, one can see that, for Td-sites C insertion into Si-C<sub>x</sub> or Si-NC<sub>x</sub>, one more C atom bonded to an existing silicon-centered cluster is always energetically more favorable (lower energy) than that carbon remains detached. The structures after relaxing are shown in supporting information (Fig. S2). Small disordering in tetrahedral Si–C<sub>n</sub> bonded structure is present, indicating the stable structure of tetrahedral Si–C<sub>x</sub> or Si–NC<sub>x</sub>.

Secondly, C insertion into octahedral Si site has to be evaluated, as presented in Table 4. The lowest energy of octahedral Si configuration Oh–Si–O<sub>4</sub>N<sub>2</sub> is considered to be the starting model. There are many possibilities for C to substitute N or O atoms. Here, we give two examples which are fully representative. One C atom inserted into an existing 6-fold site forms a  $Si-N_{2-y}C_{x+y}O_{4-x}$  or  $Si-N_2C_xO_{4-x}$  cluster. For the case of  $Si-N_{2-y}C_{x+y}O_{4-x}$ , the carbon atom number is larger than two, which increases the system energy and consequently is not favorable. The above table seems to suggest that Oh-Si site may form 6-fold coordinated cluster of Si-N<sub>2</sub>C<sub>x</sub>O<sub>4-x</sub> even with x value of 4, but with a closer look on the relaxed structure, one can see the formation of C2 dimer and its detachment from Si when more carbon is added. Fig. 8 shows a typical atomic arrangement for higher coordination number of C. A simple chemical picture is sufficient to understand this situation. Carbon atom has more available electrons to form lateral bonding, whereas for O and N counterparts, bonding options are saturated due to higher number of valence electrons on their anion status, and spinel framework already optimize their connectivity, indicating pairing up among N and O member of Oh–Si cluster is not possible. We therefore conclude that Oh-Si cluster with more than 2 carbon is impossible. As discussed above, for the tetrahedral Si site, more C atom bonded to central Si is always more stable. These calculation results strongly convince us C accumulation bonded to tetrahedral Si site forming SiC<sub>4</sub> and SiNC<sub>3</sub>.

#### 4) Structural property of doped material

Likely due to the strong covalent bond between Si and C and their bonding to neighboring atoms, 1:1 doping results in small effective cluster side of Si–C centered polyhedron. If we consider  $O_3(Al-N)Al_3$  as a sub cluster in AlON, each Al–N unit has six bonds toward 3 of O and 3 of Al atoms. As shown in Table 5, when that Al–N is replaced by Si–C pair, we can see four bonds shorten and



Fig. 8. Atomic geometry of Si–N<sub>2</sub>OC<sub>3</sub> cluster in (a) before relaxation in ideal position, and (b) after relaxation indicating C2 dimer formation. Lines between atoms merely indicate the original connectivity, calculated bond order show antibonding or nearly non-bonding between dimer C atom and Si atoms, indicating that C has been detached from central Si.

Table 5

Comparison of bond length (BL, in Angstrom) and bond order (BO, indicated in parenthesis) of atoms within  $O_3$ -AlN-Al<sub>3</sub> and  $O_3$ -SiC-Al<sub>3</sub> clusters. Among the total 7 bonds, 4 bonds shorten significantly and 3 bonds lengthen slightly, which will results in local shrinking of cluster size. It is interesting to see the bond order of bonds in  $O_3$ -SiC-Al<sub>3</sub> is always increased.

Bond	BL (BO) in AlON	BL (BO) in Si–C_AlON	BL change (BO change)
O(1)-Al/O(1)-Si	1.7487 (0.54)	1.6712 (0.58)	-4.43% (7.4%)
O(2)-Al/O(2)-Si	1.8422 (0.42)	1.7742 (0.46)	-3.69% (9.5%)
O(3)-Al/O(3)-Si	1.8422 (0.42)	1.7742 (0.46)	-3.69% (9.5%)
Al-N/Si-C	1.8166 (0.67)	1.7194 (1.16)	-5.35% (73.1%)
N-Al(1)/C-Al(1)	1.8785 (0.46)	1.9218 (0.53)	2.31% (15.2%)
N-Al(2)/C-Al(2)	1.8774 (0.51)	1.9178 (0.61)	2.15% (19.6%)
N-Al(3)/C-Al(3)	1.8774 (0.51)	1.9178 (0.61)	2.15% (19.6%)

three bonds slightly increase and all (6 + 1) bonds have bond order increased. We noted that in our cell volume relaxed calculations, no obvious volume change was observed. This might be due to (1) the doping ratio in simulation is too high, and (2) in our crystalline periodic simulation, there is no surface or grain boundary to account for the further relaxation of material. Nevertheless, increasing of bond order around defect site is favorable to achieve phosphors with better thermal stability and also results in emission redshift after Si–C doping, which is in consistence with experimental observation carried out in the present work.

# 4. Conclusions

In this work, the luminescence properties and crystal structure of AlON: Eu, xSi-C phosphors are investigated. Si-C substitution for Al–N brings more covalency, lattice rigidity and consequently results in improvement of thermal stability in AlON: Eu<sup>2+</sup> phosphors, which are proved by experimental photoluminescence results. Si and C do not distribute randomly in AlON lattice but form SiC<sub>4</sub> and SiNC<sub>3</sub> aggregation proved by NMR, which causes stalking faults and twinned structure in AlON lattice.

To explain why SiC<sub>4</sub> and SiNC<sub>3</sub> are preferable in AlON: Eu, Si–C, First-principles calculation is performed. The results show that Nconnected Al is much more likely to be replaced by Si than only-Oconnected ones. The favorite Si site is  $Td-Si-O_3N$  and Oh-Si $-O_4N_2$ . Doped Si and C form Si–C bonded pairs replacing Al–N. Further insertion of C to Td–Si is always energetically favorable, making the presence of SiC<sub>4</sub> and SiNC<sub>3</sub>. However, for Oh–Si it is energetically allowed but impossible to accommodate more C or cannot hold up a stable 6-fold coordinated Si cluster due to C2 dimer formation. Si–C doping forms double bond in the host crystalline structure and makes local structure stronger (higher bond order), which accounts for the emission redshift and better thermal stability.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2017.07.156.

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