Synthesis and characterization of luminescent properties of ceramics derived from polysilylcarbodiimides

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The luminescence properties related to the thermal polymer/ceramic conversion behavior of silicon dicarbodiimide [SDC, [Si(N=C=N)2]n] have been investigated. SDC was synthesized by the non-oxidic sol-gel condensation reaction of silicon tetra-chloride with bis(trimethylsilyl)carbodiimide. As-synthesized SDC showed no luminescence under UV light, while heat-treated SDC showed an appreciable photoluminescence (PL) and the maximum visible PL emission intensity was achieved by heat treatment at 400°C. Even after the heat treatment up to 970°C, the SDC preserved most of the N=C=N groups to keep white-gray color without distinct free carbon formation, and emitted visible blue luminescence. The 400°C-heat treated SDC exhibited a characteristic PL red emission at around 600 nm attributed to the f-f-transition of Eu³⁺.

Key-words: Non-oxidic sol-gel condensation reaction, Polymer derived ceramics, Photoluminescence, Silicon dicarbodiimide, Eu³⁺ complex

1. Introduction

Thermal decomposition of organosilicon polymers yields silicon-based ceramic materials which are denoted as polymer derived ceramics (PDCs).1) In this PDCs route, poly(organosilazanes) (PSZs) and poly(organosilylcarbodiimides) (PSCs) have been often used for synthesizing ternary SiCN ceramic-based materials.2) The polymer-derived amorphous SiCN ceramics exhibit enhanced thermal stability in terms of decomposition and/or crystallization to keep their amorphous state up to approximately 1500°C.3) They also exhibit excellent oxidation and creep resistance at very high temperatures.3,4) These findings indicate that the amorphous Si–C–N ceramics are good candidates for high temperature applications.

In addition to the excellent thermomechanical properties, luminescent properties of SiCN film have been reported.5,6) However, optical properties of PDCs have received a little attention since PDCs are generally black although there are some reports related to the luminescent properties of polymer derived SiOC,9,10) SiBOC,11) SiBN,12,13) SiCNO14) and SiCN.15,16) The reason for the black color of the PDC has been generally ascribed to the presence, in the ceramic structure of free carbon.17) For this reason, optical properties of the PDCs, especially the polymer-derived ternary SiCN materials are scarcely exploited since the absorption of visible light, which hinders their capability for the production of optical devices.

The luminescence related to the thermal polymer/ceramic conversion behavior of SiCN ternary SDC have been investigated. Moreover, luminescent properties of Eu³⁺-modified SDC has been studied and discussed from a viewpoint to develop carbodiimide derivatives as novel phosphors.
2. Experimental procedure
2.1 Synthesis of polyorganosilylcarbodiimides (PSCs)

All operations were conducted under dry argon atmosphere. The utilized glassware was stored in an oven for several hours at 120°C. All chemicals were handled using Schlenk and glove box techniques.

(1) Silicon dicarbodiimide (SDC, [Si(N=C=N)]2)

[Si(N=C=N)2]2, was synthesized following published routes shown in Eq. (1).

\[ \text{at room temperature} \]

2SiCl4 (4.98 mL, 0.043 mol) in dried THF (5.93 mL) was added dropwise to a stirred mixture of diamide (C2H4N4), 1,1,1,3,3,3-hexamethyldisilazane and a catalytic amount of ammonium sulfate ([NH4]2SO4) by heating to reflux for 12 h and distilling over a Vigreux column at 164°C. Silicon tetrachloride (SiCl4), pyridine, and dried trihydrofuran (THF) were commercial products.

\[ n\text{SiCl}_4 + 2n\text{CH}_3\text{Cl} \rightarrow [\text{Si}(\text{N} = \text{C} = \text{N})]_2 + 4n\text{(CH}_3\text{)}_3\text{SiCl} \]  

At room temperature, SiCl4 (4.98 mL, 0.043 mol) was mixed with dried THF (5.93 mL) and added dropwise to a stirred mixture of bis(trimethylsilyl)carbodiimide (20 mL, 0.088 mol) and pyridine (1.94 mL, 0.024 mol) in a 100 mL Schlenk flask. The mixture was refluxed at 70°C for 1 h. After removal of the solvent and Me3SiCl by distillation, fine white powder was obtained.

(2) Eu3+-modified SDC ([Si(N=C=N)2]2-Eu3+]

After the reaction, EuCl3 (0.111 g, the molar ratio of Eu3+ to [Si(N=C=N)2]2) of 1 mol %) was dissolved in THF (5.93 mL) in a 100 mL Schlenk flask. To the mixture, bis(trimethylsilyl)carbodiimide (20.13 mL, 0.089 mol) and pyridine (1.94 mL, 0.024 mol) were added, then, SiCl4 (4.98 mL, 0.043 mol) in dried THF (5.93 mL) was added dropwise at room temperature. The mixture was refluxed at 70°C for 6 h. After removal of (CH3)3SiCl, [Si(N=C=N)2]2-Eu3+ was isolated as a white powder.

2.2 Heat treatment

(1) Conversion into ω-silicondicarbodiimide (ω-Si2C3N4)

By using a conventional tube furnace, the synthesized polymers ([Si(N=C=N)2]2, [Si(N=C=N)2]2-Eu3+) were heat-treated under vacuum from room temperature to 350°C with 1.5 h holding time. Then, an argon (Ar) gas was introduced into the tube furnace at 350°C and the temperature was raised up to the desired temperatures ranging from 200 to 700°C with 0.7 h holding time at the maximum temperature under Ar flow (heating rate of 100°C/h). After the heat-treatment, the samples were cooled down in a furnace.

(2) Conversion into silicon(carbodiimide)nitride (Si3C3N4)

The precursor gels ([Si(N=C=N)2]2, [Si(N=C=N)2]2-Eu3+) were calcined under vacuum from room temperature to 380°C with 2.0 h holding time, subsequently the temperature was lowered to room temperature. Then, the temperature was raised up to 970°C under Ar atmosphere. Further heating to 600°C within 3 h was carried out and the heat-treatment was completed by cooling the samples to room temperature.

2.3 Characterization

Powder X-ray diffraction (XRD) measurements were performed at room temperature with Cu Kα radiation (Bruker D8 Advance, Germany). The samples were placed in holders filled with argon in order to avoid contact with air. Fourier transform infra-red spectroscopy (FT-IR) spectra were recorded in air using Attenuated Total Reflection (ATR) on an Ivan 670 IR Spectrometer (Varian, USA) with a spectral resolution of 2.0 cm⁻¹.

The PL emission/excitation measurements were performed at room temperature in air. The spectra were recorded on a fluorescence spectrophotometer (F-7000, Hitachi, Japan) using a xenon lamp as the excitation source. The samples were measured in powder or rubber-like form in 1 mm precision cells made of Quartz (T-1-UV-1, Tosoh Quartz Inc., Japan). UV–vis diffuse reflectance/absorption spectra were recorded by a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer (Perkin-Elmer GmbH, Germany) using an integrating sphere. The samples were measured in powder form in 1 mm precision cells made of Quartz.

The thermal transformation of SDC gel up to 1400°C was studied by means of TGA/MS with a simultaneous thermal analysis device (STA 449C Jupiter, Netzsch, Germany) coupled with a quadrupole mass spectrometer (QMS 403C Aëolos, Netzsch, Germany). The measurements were done under flowing argon, with a heating rate of 240°C/h. The quadrupole mass spectrometer is attached to the TG device by means of a capillary coupling (1.5 m in length, diameter 0.15 mm and heated at 280°C). ²⁵Si liquid state NMR spectra were measured on 300 MHz Avance III Spectrometer (internal name AR300). The preparation of the samples was done under inert atmosphere (Ar) in order to avoid the hydrolysis reaction. The liquid sample (0.2 ml) was mixed with benzene-D₆ (C₆D₆) solvent (0.4 ml) in Norell XR55 NMR tubes.

3. Results and discussion

3.1 The chemical structure and the mechanism of luminescence related to the polymer/ceramics conversion behavior of SDC

Figure 1 shows FT-IR spectra of SDC gel as-synthesized and after heat-treatment at different temperatures under Ar and cooling to room temperature. The as-synthesized gel exhibits the typical characteristics of silicon carbodiimide. ¹⁹,²³,²⁷-²⁹ The two strong absorption bands located at 2141 and 764 cm⁻¹ belong to the vibration modes of ν₃(N=N) and ν₁(N≡C), respectively, confirming that Si is coordinated to N=C=N units in the products. The band at 571 cm⁻¹ is assigned to ν(Si–C–N) and ν(Si–Cl) groups. The absorption band at 1254 cm⁻¹ is due to Si–C₃H₄ groups, suggesting the presence of –Si(CH₃)₃ end groups in the silicon carbodiimide network. It may also arise from residual trimethylchlorosilane formed as a by-product in the SDC gel synthesis shown in Eq. (1). The weak absorption bands at 1090, 963 and 846 cm⁻¹ correspond to Si–O vibrations, which are due to a slight hydrolysis of the products. This indicates the very high sensitivity of SDC towards moisture. After heat-treatment at and below 400°C, the relative intensity of Si–C₃H₄ vibration decreased and the vibration bands are no longer detected in the sample heat-treated at 500°C, while the rest of the spectrum at and below 700°C corresponds to that of the starting material. It means that the amount of the trimethylsilyl groups decreased by evaporation of the residual (CH₃)₃Si–N=C=N–Si(CH₃)₃. ³⁰

The FT-IR spectrum of the sample heat-treated at 970°C presents the characteristic bands of carbodiimide groups at 2160 cm⁻¹ [ν₁(N≡C=N)] and 774 cm⁻¹ [δ(N≡C=N)] respectively. In this case, additional vibration bands can be detected for the Si–N bonds at 933, 889, 560 and 513 cm⁻¹.

Thermogravimetric (TG) analysis [mass loss x (%)] and differential thermal analysis (DTA (µV/mg)) of SDC gel, as well as the monitoring of the heat-treatment under Ar by mass spectrometry of the product gases N₂ and C₂N₂, heating rate: 4°C min⁻¹ are
shown in Fig. 2. At higher temperatures SiC$_2$N$_4$ reveals a weight loss of about 20% and the gaseous products of cyanogen (C$_2$N$_2$) and nitrogen (N$_2$) were detected by mass spectrometry. Thus, the decomposition reaction gives Si$_2$CN$_4$ phase and the formal reaction equation can be derived:

$$4\text{SiC}_2\text{N}_4 \rightarrow 2\text{Si}_2\text{C}_4\text{N}_4 + 3\text{C}_2\text{N}_2 + \text{N}_2 \quad (2)$$

In the DTA, two exothermal peaks at 985 and 998°C can be assigned to decomposition of the SiC$_2$N$_4$ phase and crystallization of Si$_2$CN$_4$, respectively. The appearance of the Si–N bonds is due to the decomposition of carbodiimide group and rearrangement during heat-treatment.$^{(19)\text{--}23)\text{,}27)\text{,}28)}$ in FT-IR.

XRD patterns of SDC gel heat-treated at different temperatures are shown in Fig. 3. SDC gel remains X-ray amorphous up to 300°C. The initial crystallization begins at 400°C to give α-SiC$_2$N$_4$, then, Si$_2$CN$_4$ is detected at 970°C by the thermal decomposition of α-SiC$_2$N$_4$. These XRD patterns and the crystallization behavior are in good agreement with the previous reports.$^{(21)\text{,}23)\text{) }}$

In Fig. 4, SDC gel as-synthesized and after heat-treatment at different temperatures are shown under white and UV light (254 and 366 nm). The powder color of SDC gel was white and that of the 970°C-heat treated SDC (Si$_2$CN$_4$) was found to keep color as whitish gray. To take into account of the results of FT-IR, TGA-MS and XRD analyses, preservation of the N=C=N groups during heat-treatment at and below 1000°C results in restricting free carbon formation, which leading to keeping the color of the SDC-derived powder as white. However, SDC exposed to temperatures above 400°C, the powder color of the generated α-SiC$_2$N$_4$ changed greatly depending on the heat-treatment temperature. The α-SiC$_2$N$_4$ is probably a distorted structure with a topology similar to the β-SiC$_2$N$_4$. Therefore, the change in the powder color is thought to be due to interactions or errors in the crystal structure of α-SiC$_2$N$_4$. The stresses induced by the interactions or errors could lead to the formation of lattice defects such as vacancies and change of a particle size, which caused the color change of the obtained powder sample.$^{(23)\text{) }}$

PL emission from the as-synthesized SDC gel was not observed under UV lights. On the other hand, the heat-treated SDC showed an appreciable PL emission and the maximum visible PL emission intensity under UV light at 254 nm was...
achieved by the heat-treatment at 400°C. Moreover, PL emission was observed for the 970°C-heat treated SDC and it showed blue emission under UV light at 366 nm (Fig. 4).

UV–Vis, PL emission excited at 254 nm and PL excitation (\(\lambda_{\text{exc}} = \) Peak PL emission intensity) spectra of SDC gel as synthesized and after heat-treatment at different temperatures are shown in Fig. 5. In UV–Vis spectra, at around 210 nm, all the samples have the absorption of N=C=N groups. Another absorption peak centered at around 250 nm of the SDC gel is due to a residual bis(trimethylsilyl)carbodiimide [Fig. 5(a)]. The highest PL emission intensity excited at 254 nm was achieved for the 400°C-heat treated SDC [Fig. 5(b)], and the result is in agreement with the PL luminescence photographs (Fig. 4). There are two broad excitation peaks in all the spectra of heat-treated SDCs [Fig. 5(c)]. The PL emission and excitation wavelengths corresponding to the maximum excitation and emission peaks are listed in Table 1.

To examine the PL properties of the heat-treated SDCs, UV–Vis, PL emission and PL excitation spectra of the 400°C and 970°C-heat treated SDC were selected and shown in Fig. 6 and Fig. 7, respectively. As shown in Fig. 6, the 400°C-heat treated SDC exhibited the intense luminescence at 401 nm (\(\lambda_{\text{em}} = 281\) nm) and 438 nm (\(\lambda_{\text{em}} = 379\) nm), while there was no PL emission excited by the N=C=N group-derived host absorption at 214 nm. Similar to the results shown above, the 970°C-heat treated SDC showed the luminescence at 392 nm (\(\lambda_{\text{em}} = 288\) nm) and 395 nm (\(\lambda_{\text{em}} = 366\) nm), although the PL emission wasn’t observed by the excitation at the host absorption of 213 nm (Fig. 7).

To clarify the origin of the luminescence observed for the heat-treated SDCs, it is necessary to consider the structural changes and rearrangements associated with the heat-treatment temperature. During the heat-treatment, the polymeric structure undergoes a transformation into a three-dimensional solid network structure (ceramic). Therefore, as the temperature increases, the formation of defects (e.g. dangling bonds) could be occurred. In the spectrum of 400°C-heat treated SDC, there were two excitation peaks and each excitation wavelengths lead to the different PL emission. At and below 700°C, the PL emission peaks located at longer wavelength (435–473 nm) appeared with the crystallization process of \(\alpha\)-SiC\(_2\)N\(_4\) phase by increasing the heat-treatment temperature, while those located at the shorter wavelengths (385–401 nm) in the PL emission disappeared.

![Fig. 4](imageURL)  Photographs representing SDC gel and after heat-treatment at different temperatures under white, and under UV light at 254 and 366 nm (The origin of the blue emission from the right side of tubes under UV light was a sealing tape).

![Fig. 5](imageURL)  (a) UV–Vis, (b) PL emission (\(\lambda_{\text{em}} = 254\) nm) and (c) PL excitation (\(\lambda_{\text{exc}} = \) Peak PL emission intensity) spectra of SDC gel and after heat-treatment at different temperatures.

**Table 1.** PL emission and excitation wavelengths corresponding to the maximum excitation and emission peaks

| SDC     | PL excitation wavelength (nm) | PL emission wavelength (nm) |
|---------|-------------------------------|----------------------------|
| As-prepared | 283                           | 385                        |
| 200°C   | 330                           | 385                        |
| 300°C   | 278                           | 395                        |
| 400°C   | 351                           | 397                        |
| 500°C   | 281                           | 401                        |
| 600°C   | 379                           | 438                        |
| 700°C   | 287                           | 435                        |
| 970°C   | 377                           | 438                        |
| 970°C   | 289                           | 473                        |
| 970°C   | 365                           | 473                        |
| 970°C   | 288                           | 392                        |
| 970°C   | 366                           | 395                        |
Thus, it seems that the PL emission at longer wavelengths is caused by the intrinsic defects formed during the α-SiC2N4 crystallization process. On the other hand, there are two possible reasons for the PL emission at the shorter wavelengths: (i) some defects (Si, C or N dangling bond, \(^{9,10,18,30,31}\)) formed by decomposition or elimination of the trimethylsilyl end groups, and (ii) structure defects of Si–O–Si formed by accidentally contaminated oxygen.\(^{32,33}\)

In the spectrum of 970°C-heat treated SDC, the dominant PL excitation peak was observed at 366 nm, and the related PL emission peak was detected at 395 nm despite the different excitation wavelengths (\(\lambda_{\text{ex}} = 366, \) 288 nm). Therefore, it is assumed that the defects related to the each PL center could be formed by the decomposition of N=C=N groups in α-SiC2N4 to give Si2CN4.

(2) The material structure and luminescent properties of Eu\(^{3+}\)-modified SDC

Photographs of Eu\(^{3+}\)-modified SDC gel (SDC:Eu\(^{3+}\)), under white or UV light at 254 nm are shown in Fig. 8. The SDC:Eu\(^{3+}\) exhibited the intense red emission.

To investigate the mechanism for this red luminescence, EuCl\(_3\) used as a source of Eu\(^{3+}\) and bis(trimethylsilyl)carbodiimide were mixed, and tried to proceed the reaction analogously as the formation of SDC [Eq. (3)].

\[
n\text{EuCl}_3 + 1.5n(\text{CH}_3)_3\text{Si} - \text{N} = \text{C} = \text{N} - \text{Si}(\text{CH}_3)_3 \rightarrow [\text{Eu(N=\text{C}=\text{N})_3\text{Si}]} + 3n(\text{CH}_3)_3\text{SiCl}
\]

After addition of the reaction catalyst of pyridine, the yellowish precipitates formed immediately. The yellowish precipitates recovered by distilling off the liquids also showed intense red luminescence under UV light at 254 nm (Fig. 8).

The liquid state\(^{29}\)Si NMR spectra of the mixture before and after 6 h reflux are presented in Fig. 9. There is only one signal peak that represents Si(\(\text{CH}_3\)\)_3\text{N}CN (\(-1.11\) ppm) before reflux.\(^{25}\) After refluxing for 6 h, the spectrum exhibited the same signal peak due to the Si(\(\text{CH}_3\)\)_3\text{N}CN without a peak at 29.94 ppm assigned to the reaction by-product of (\(\text{CH}_3\)\)_3\text{SiCl}.\(^{23}\) Therefore, the expected reaction didn’t proceed.

To study the interaction between EuCl\(_3\) and bis(trimethylsilyl)carbodiimide to yield the yellowish precipitates, XRD and FT-IR analyses were performed on the recovered mixture after the refluxing with catalytic amount of pyridine, and that after heat treatment at 200°C. As shown in Fig. 10, the recovered mixture [Fig. 10(a)] showed X-ray amorphous without distinct diffraction peaks derived from EuCl\(_3\) [Fig. 10(b)], while this sample exhibited characteristic carbodiimide (N=C=N) and/or cyanamide (N=C≡N) absorption bands at about 2000 cm\(^{-1}\)\(^{23}\).
After heat treatment at 200°C, the XRD pattern revealed the formation of EuCl₂ (the diffraction peaks were identical to those of JCPDS Card No. 032-0371). In the FT-IR spectrum of the 200°C heat-treated sample [Fig. 11(b)], the characteristic absorption peaks at about 2000 cm⁻¹ disappeared and new peaks appeared at 1700–1400 cm⁻¹, which was thought to be due to the formation of partly organic conjugated system.

Based on the results shown above, EuCl₃ and bis(trimethylsilyl)carbodiimide could form a complex, which leading to the red emission under the UV right. The complex was thermally unstable and decomposed to give EuCl₂ crystallites and free C. As a result, after the heat-treatment at 200°C, the color of the sample powder turned to be black (Fig. 8).

Figure 12 shows the spectra of UV–Vis absorption, and PL emission excited at 254 nm recorded for the SDC:Eu³⁺ and the recovered reaction mixture of EuCl₃ and bis(trimethylsilyl)carbodiimide (here after recovered reaction mixture).

In addition to the absorption band due to the bis(trimethylsilyl)carbodiimide at around 302 nm, the recovered reaction mixture exhibited an additional broad absorption band at around 302 nm assigned to N=O groups, while the small peaks over 350 to 500 nm wavelengths in this spectrum are due to the intra-configurational f-f transitions of Eu³⁺. In the spectrum of the SDC:Eu³⁺, the absorption at around 302 nm due to the N=O groups was also detected as a weak and broad band [Fig. 12(a)]. During the interaction process for the complex formation between EuCl₃ and bis(trimethylsilyl)carbodiimide, N=O groups were thought to be in-situ formed by the tautomerization of N=O groups to some extent.

In the PL emission spectra excited at 254 nm [Fig. 12 (b)], both the SDC:Eu³⁺ and the recovered reaction mixture exhibited characteristic emission of Eu³⁺ due to the f-f transition. The intense
peak at 593 nm detected for the both samples was due to the $^{3}\text{D}_{0}\rightarrow\text{T}_{1}$ transition, while the peaks at 612 nm in the SDC:Eu$^{3+}$ and at 613 nm in the recovered reaction mixture were assigned to $^{3}\text{D}_{0}\rightarrow\text{T}_{2}$ transition. The PL red emission ($\lambda_{\text{em}} = 254$ nm) of the complex could be successfully achieved by the sufficient absorption at around 254 nm of the bis(trimethylsilyl)carbodi-imide which could be a counterpart of EuCl$_3$ in the complex.

4. Conclusions

The chemical structure and the mechanism of luminescence properties related to the thermal polymer/ceramics conversion behavior of SDC were investigated. Moreover, the chemical structure and luminescent properties of Eu$^{3+}$-modified SDC was also studied. The results are summarized as follows:

(1) The powder color of SDC gel was white and that of the 970°C-heated treated SDC was found to keep color as whitish gray due to the restricting free carbon formation by preserving N=C=N groups.

(2) PL emission from the as-synthesized SDC gel was not observed under UV light at 254 nm, while the heat-treated SDC showed an appreciable PL emission, and the 400°C-heated treated SDC exhibited the highest PL emission intensity.

(3) The 400°C-heated treated SDC exhibited the intense luminescence at 401 nm ($\lambda_{\text{em}} = 281$ nm) and 438 nm ($\lambda_{\text{em}} = 379$ nm), while there was no PL emission excited by the N=C=N group-derived host absorption at 214 nm. Therefore, the PL properties could be correlated to the formation of intrinsic defects by the crystallization of $\alpha$-SiC$_2$N$_2$ phase, other defects formed by decomposition or elimination of the trimethylsilyl end groups, and structure defects of Si–O–Si formed by oxygen contamination during the heat treatment.

(4) PL emission observed for the 970°C-heated treated SDC under UV light at 366 nm was also thought to be due to the PL center related to the defects formed by the decomposition of N=C=N groups in $\alpha$-SiC$_2$N$_2$ to give Si$_4$C$_2$N$_2$.

(5) Under the UV light at 254 nm, Eu$^{3+}$-modified SDC exhibited a characteristic red luminescence around 600 nm attributed to the $f$-$f$-transition of Eu$^{3+}$. The results of XRD analysis, FT-IR and liquid state $^{29}$Si NMR spectroscopic analyses indicated the complex formation between EuCl$_3$ and bis(trimethylsilyl)carbodi-imide, and the observed PL emission was achieved by the sufficient absorption at around 254 nm of the bis(trimethylsilyl)-carbodi-imide in the complex.

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