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Novel synthesis of Eu-doped SiAlON luminescent materials from a preceramic polymer and nano-sized fillers



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ABSTRACT

A commercial polysilazane, mixed with nano-sized fillers particles, has been used for the first time for the preparation of Eu-doped β' - and α' -SiAlON-based powders, exhibiting yellow, green and blue luminescence under blue or near UV excitation, depending on processing conditions. β' -Phase was obtained by mixing the preceramic polymer with both γ -Al₂O₃ and Si₃N₄ nanoparticles, whereas the Ca α -phase was achieved by adding γ -Al₂O₃ and CaCO₃ nanoparticles. Rare-earth ions were provided by Eu₂O₃ nano-particles.

The reduction of Eu^{3+} into Eu^{2+} incorporated in SiAlON was favored by the presence of carbon derived from the pyrolysis of the preceramic polymers. The nanometric distribution of filler materials and the high yield of the selected preceramic polymers in terms of Si and N atoms led to the formation of the desired phases at relatively low firing temperatures (e.g. 3 h at 1550–1600 °C in pure nitrogen).

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1. Introduction

After extensive investigations supporting their use as structural ceramics [1,2] SiAlONs have found a very promising secondary application as luminescent materials to be used in modern LED devices. In fact, rare earth oxides, previously used simply as sintering aids, can provide luminescence by conversion of UV or blue light. Strong luminescence can be provided not only by classical SiAlON phases, such as β' and α' , but also by other oxynitride phases, owing to their chemical and physical characteristics (they mostly contain covalent chemical bonds); the covalent bonding gives rise to a strong nephelauxetic effect (i.e. electron cloud expansion), reducing the energy of the excited state of 5d electrons of rare

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earth activators (e.g. Eu^{2+} , Ce^{3+}) [3]. In addition, because the formal charge of N (-3) is higher than that of O (-2), the crystal field splitting of 5d levels will be larger [4]. This results in long excitation/emission wavelengths and low thermal quenching [4–10] which cannot be achieved in conventional phosphors.

It has recently been shown that silicate ceramics and β' -SiAlON can be produced by a novel approach, leading to high yields of the desired phases at generally low temperatures, for very simple processing conditions. Specifically, oxide and nitride particles are introduced as fillers in preceramic polymers, such as polysiloxanes and polysilazanes, which transform into a silica, SiOC or SiCN ceramic residue upon thermal treatment in air or nitrogen [11–13]. The production of the desired phases is due to the reaction between this polymer-derived ceramic residue and the introduced fillers, which is favored by their nanometric size. The formation of β' -SiAlON is generally more complicated than the production of silicate phases, since C, present in the SiOC or SiCN ceramic residue generated when processing in inert atmosphere, removes some of the oxygen present in the material, forming CO, and promotes nitridation, according to the following reaction schemes [12,13]:

 $SiOC_{(frompolymer)} + AlN_{(filler)} + N_{2(atmosphere)} \rightarrow SiAlON + CO_{(gas)}$

 $SiCN_{(frompolymer)} + Al_2O_{3(filler)} + N_{2(atmosphere)} \rightarrow SiAlON + CO_{(gas)}$

Achieving a precise balance among the different elements present is therefore crucial, and phase purity may be compromised by an excessive C or O content. Besides CO, gaseous SiO

Table 1

Formulations for preceramic-polymer-derived SiAlON phosphors.

Component	Supplier	Content (wt%)	
		S1 formulation	S2 formulation
HTT1800	KiON HTT 1800, Clariant Advanced Materials GmbH, Germany	64.9	65.4
γ-Al ₂ O ₃ nanopowders, 13 nm	Evonik Industries AG, Essen, Germany	5.9	17.3
Amorphous Si ₃ N ₄ nanopowders, 20 nm	Goodfellows, Huntingdon, UK	28.4	-
CaCO ₃ nanopowders, 90 nm	PlasmaChem GmbH, Berlin, Germany	_	16.7
Eu ₂ O ₃ nanopowders, 45–60 nm	Cometox, Milan, Italy	0.8	0.6

may also form; moreover, C can be either present in clusters (so called "free-carbon") or combined with Si as SiC (amorphous or nano-crystalline), in turn promoting other reactions [12]. Several processing parameters, in particular partial pressure of gaseous species, influence the chemical compositions as well as the microstructures in the polymer-derived SiOC and SiCN ceramics, including the composition and molecular structure of the preceramic precursor, the pyrolysis atmosphere and schedule (maximum temperature, dwelling time) as well as presence and reactivity of added fillers [14]. Control of the interplay of all these parameters affecting the characteristics of the resulting ceramic material when using preceramic polymers is certainly a challenge, but it also provides powerful opportunities for achieving different results based on the modification of the processing parameters. Moreover, a further advantage of preceramic polymers is that they can be easily processed into different shapes (coatings, fibers, highly porous or dense parts), therefore enabling the fabrication of innovative functional ceramic components.

Recently, it has been shown that optimized formulations, based on polysilazanes, can lead to almost pure β' -SiAlON (described by the formula Si_{6-z}Al_zO_zN_{8-z}, with *z*, representing the number of Si—N bonds replaced by Al—O bonds) [13]; the present paper represents a preliminary attempt to transfer this finding to the preparation of luminescent materials based on rare-earth doped β -SiAlON. In addition, it will be shown that the proposed approach of adding nano-sized fillers to preceramic polymers can produce even the α' -SiAlON phase (described by the formula $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, where *m* is the number of Si—N bonds replaced by Al—N bonds, n is the number of Si—N bonds replaced by Al—O bonds, and x > 0 is *m* divided by the valency of the M cation [15]), which is an excellent host lattice for doping with luminescent rare-earth ions [6].

2. Experimental procedure

Mixtures comprising a commercial polysilazane (KiON HTT 1800, Clariant Advanced Materials GmbH, Germany) and several types of nano-sized filler particles were processed according to the procedure previously developed for simple polysilazane/ γ -Al₂O₃ mixtures [13]. The nano-sized particles, weighed according to the proportions reported in Table 1, were dried overnight at 200 °C in air, and then immediately inserted into a glass container under flowing nitrogen, to avoid surface adsorption of moisture. For each formulation studied, a polysilazane/hexane solution (approximately 20 wt% solid content) was prepared aside in a beaker, and then rapidly inserted into the glass container with the nanosized powders, thus producing a dispersion with a solid content of approximately 30 wt%. Magnetic stirring and ultrasonication were necessary to obtain homogeneous dispersions which were stable for at least 1 h. The ceramic yield in N₂ of the HTT1800 polymer (with the composition $SiC_{0.66}N_{0.6}O_{0.03}$) was 70 wt% [16,17].

The dispersions for both S1 and S2 formulations were poured into aluminum containers and immediately cured at 300 °C for 1 h in a tube furnace under flowing nitrogen. After the curing step, the samples were placed onto alumina trays and pyrolyzed in flowing N₂ (99.99% pure) for 1–3 h in the 1400–1600 °C temperature range, with a 10 °C/min heating and cooling rate, in an alumina tube furnace. Before inserting the samples into the tube, N₂ was flown for 30 min at 200 °C to reduce the humidity content inside the tube. S1 formulation was additionally tested in a more reducing atmosphere (95% N₂–5% H₂); in this case the cured polymer mixture was first pre-pyrolyzed at 600 °C in flowing N₂ and then fired for 1 h in the 1500–1700 °C temperature range in N₂–H₂ atmosphere (heating rate of 3 °C/min; cooling rate of 1 °C/min, above 700 °C, and 3 °C/min below).

At the end of the thermal treatments, the ceramic residue of each formulation, in form of coarse powders, was ground for 30 min in air, in a planetary mill (agate container with agate balls).

Powdered samples were investigated by X-ray diffraction (XRD, Bruker AXS D8 Advance; Bruker, Karlsruhe, Germany), operating with CuK α radiation (0.15418 nm). A semi-automatic phase identification was performed by using the Match! program package (Crystal Impact Gmbh, Bonn, Germany) supported by the PDF-2 crystallographic database (Powder Diffraction File-2; ICDD, Newtown Square, PA).

Characterization of the luminescence characteristics was conducted by means of a spectrofluorometer (FP-6300, JASCO Ltd., Great Dunmow, UK and Perkin-Elmer LS 50B, Waltham, MA, USA), on powders ground and sieved to a maximum diameter of $20 \,\mu$ m and dispersed in distilled water (for testing with FP-6300) or pressed in a sample holder (for testing with LS 50B).

3. Results and discussion

The formulations reported in Table 1, S1 and S2, were conceived to form of SiAlON ceramics according to the following reactions:

$$\begin{split} &3.5SiC_{0.66}N_{0.6}O_{0.03} + 0.7Si_3N_4 + 0.2Al_2O_3 + 0.008Eu_2O_3 + 1.34N_2 \\ &\rightarrow Eu_{0.016}Si_{5.6}Al_{0.4}O_{0.4}N_{7.6} + 0.33CO + 1.98C_{[excess]} \end{split} \tag{1}$$

 $9SiC_{0.66}N_{0.6}O_{0.03} + 1.47CaO + 1.5Al_2O_3 + 0.015Eu_2O_3 + 5.3N_2$ $\Rightarrow Cat = 5icAl_2N_{16} + 5.9CO + 0.02O_{16} + 5.3N_2$ (2)

$$\rightarrow \text{Ca}_{1.47}\text{Eu}_{0.03}\text{SI}_9\text{AI}_3\text{N}_{16} + 5.9\text{CO} + 0.02\text{O}_{2[\text{excess}]}$$
(2)

The expected products, i.e. Eu-doped β' -SiAlON (z = 0.4, for S1) and Ca α' -SiAlON (x = 1.47, m = 3, n = 0, for S2), are known as efficient phosphors [6,8].

The β' -SiAlON-based formulation, S1, requires some explanations in the light of previous work on polymer-derived β' -SiAlON using preceramic polymers and nano-sized fillers [12,13]. Polysilazanes containing Al₂O₃ nano-sized particles can lead to mainly phase-pure β' -SiAlON, especially when high polymer/filler ratios are used. High polymer/filler ratios allow to avoid the presence of unreacted alumina deriving from the loss of Si atoms due to the formation of SiO gas or of SiC as secondary phases [13]. SiC contaminations can be effectively removed by reducing the overall



Fig. 1. X-ray diffraction patterns for S1 samples heat treated in different conditions of time, temperature and atmosphere.

C content of the ceramic residue of the preceramic polymer. This was achieved by using a mixture of polysilazanes, instead of a single polymer: a poly-organo-silazane (PSZ 20, similar to the one used also in this investigation), was mixed with a poly-silazane not containing any carbon (perhydropolysilazane, PHPS) [13]. This processing approach based on two polysilazanes, although successful, is quite difficult to be reproduced, considering the observed high sensitivity to slight variations in the processing conditions (temperature, humidity, etc.) that leads to undesired secondary phases.

The mixture of composition S1 was formulated in order to provide a more robust processing strategy; amorphous silicon nitride was introduced as nano-sized filler with the aim of (i) replacing PHPS in yielding both Si and N; therefore, diluting the C content present in the ceramic residue deriving from the pyrolysis of the HTT1800 silazane and (ii) leading to a β' -SiAlON with a low *z* value, preferred for phosphors [8,9].

Eq. (1) shows that the oxygen content, even considering the introduction of a secondary oxide, Eu₂O₃, obviously intended to provide luminescence, is not adequate for a complete removal of C as CO gas. In any case, secondary SiC crystals were not observed in the produced ceramic material. As illustrated in Fig. 1a, β -phase, i.e. the desired β' -SiAlON (with a low *z* value in between 0 and 1), is the only crystalline phase present after heat treatment of pre-pyrolyzed powders, in flowing N₂, at the relatively low temperature of 1600 °C, for 3 h. The β -phase (with higher *z* value, see later) is actually recognizable already at 1400 °C, together with some α -phase.

The change in the firing atmosphere from pure nitrogen to N_2/H_2 had a remarkable effect on the phase assemblage of the resulting ceramic. In Fig. 1b, we can observe, from the intensity of the main peaks of both α - and β -SiAlON phases that the α -phase is present in a lower amount after heating at 1500 °C, compared to firing in N_2 . At higher temperature, however, while the α -phase almost disappeared after heating at 1600 °C for 1 h in N_2 , it remained present in N_2/H_2 atmosphere even after a treatment at 1700 °C.

Fig. 2a reports the luminescence characteristics of β -phase ceramic obtained by treatment of the S1 formulation in flowing N₂.

In all cases, the absence of line emission in the red region (sharp lines between 580 and 650 nm) is considered as an evidence of the reduction of Eu³⁺ into Eu²⁺ [8]. Whereas the sample fired at 1600 °C for 1 h in N₂ atmosphere does not exhibit virtually any luminescence, the sample fired for 3 h shows a green emission, therefore behaving quite similarly, as expected, to an Eu-doped β' -SiAlON (with low *z* value), as reported by Ryu et al. [8]. The emission spectrum (right graph of Fig. 2a) had a narrow band centered at 534 nm, when the sample was excited at 454 nm (frequency at which the absorption is maximized, as shown by the left graph of Fig. 2a). Interestingly, the bandwidth (FWHM, of about 20 nm) was much narrower than in previous studies (~60 nm, according to Xie et al. [18]). The excitation peak and the emission peak centered at 490 and 685 nm are not yet clear and deserve further investigation.

The powders after firing at $1600 \,^{\circ}$ C for 1 h, in N₂ atmosphere, exhibited a light gray-green color and an emission in the green. However, the color was not homogeneous, with light green granules accompanied by dark gray-black ones that could be due to C-rich areas, expected on the basis of the C excess in Eq. (1).

The presence of an excess of C led to investigating heat treatments in an alternative atmosphere, i.e. N_2/H_2 . Hydrogen gas is suitable for removing amorphous carbon, as already reported for the purification of CNTs (by evolution of CH₄) [19].

The excitation and emission spectra of the product of S1 formulation heat treated in N₂/H₂, shown in Fig. 2b, are significantly different from the spectra observed for Eu: β '-SiAlON (Fig. 2a). Emission spectra were measured with an excitation at the wavelengths of maximum excitation (arrows in the left graph in Fig. 2b, located at about 380, 320, 330 nm). The samples fired at 1500 and 1600 °C (for 1 h) had quite similar excitation spectra (main peaks located at 265 and 320–330 nm) and a main emission peak centered at about 425 nm (more intense for the sample fired at 1500 °C), i.e. in the blue region. Both excitation and emission spectra are thus consistent with the presence of Eu²⁺: β '-SiAlON phase with a high *z*-value (*z*= 3–4), as reported in the literature [20].

The sample fired at $1700 \,^{\circ}$ C (for 1 h) was significantly different in both excitation and emission behavior. The excitation/emission characteristics of the material fired at $1700 \,^{\circ}$ C were more similar



Fig. 2. Luminescence spectra for S1 samples heat treated at different temperatures in (a) N_2 and (b) N_2/H_2 .

to Eu²⁺-doped Ca- α' -SiAlON than to Eu²⁺-doped β' -SiAlON [6]; in particular, the emission was in the yellow region, being centered at 572 nm, for a sample excited at 381 nm. In the emission spectrum also a low intensity band emission at about 660 nm can be observed, indicating the possible presence of traces of a pure nitride phase, such as Eu₂Si₅N₈ [21].

An (at least partial) explanation of the observed optical behavior comes from a more in depth analysis of the diffraction data. Fig. 3 reports a comparison of the most significant diffraction data, for treatments in both N₂ and N₂/H₂, with the reference diffraction pattern for β -Si₃N₄ (PDF#82-0710). Considering the asymmetry in the peaks, the peaks previously attributed to β -phase can be interpreted as deriving from the overlapping of contributions from two phases, consisting of a relatively Al-rich high *z*-value SiAlON phase and a secondary one, Al-poor low *z*-value SiAlON phase (effectively close to the reference, with a X-ray diffraction pattern close to that of β -Si₃N₄). The Al-rich high *z*-value phase could be due to the relatively easy reaction between the polymer and the nano-sized Al₂O₃ (yielding β '-SiAlON already at 1400 °C). The Al-poor low *z*-value phase could be due to unreacted Si₃N₄ filler.

The decreasing *z* value of the Al-rich β -phase with increasing heating time (at 1600 °C in N₂, *z* went from about 2 – PDF#76-0599 – for 1h treatment to about 1 – PDF#48-1615 – for 3 h treatment) or heating temperature (for treatment in N₂/H₂ *z* went from 3 – PDF#76-0597 – at 1500 °C, to 1 – PDF#48-1615 – at 1700 °C) can be attributed to an increased incorporation into the SiAlON phase of the second filler, i.e. silicon nitride, or to an interfacial reaction among polymer-derived residual SiCNO amorphous phase and first developed SiAlON grains (SiAlON_{high z} + SiCNO_{matrix} \rightarrow SiAlON_{low z} + CO), as proposed for previously reported polysilazane-derived SiAlON [13].

The different evolution of samples treated in N_2 or in N_2/H_2 could be associated to a specific action of hydrogen gas. The reduction of the overall carbon content, in the ceramic residue, probably impeded the interfacial reaction, with additional evolution of SiO gas from the decomposition of the residual SiCNO amorphous phase.

Considering the presence of more than one β -phase, the distribution and local coordination of Eu²⁺ ions are not so straightforward. We can posit that, in the sample fired in N₂/H₂ at 1500 °C, Eu²⁺ ions concentrated mainly in the β -phase with $z \approx 3$



Fig. 3. (a) Refined XRD studies for S1 samples heat treated in both N₂ and N₂/H₂ and (b) high magnification details of selected samples.

(PDF#76-0597), thus justifying the observed blue emission. At 1700 °C instead, the formation of some Eu-doped α' -SiAlON is believed to occur. For this sample, the XRD peaks of the α -phase of Fig. 1b should be associated to α' -SiAlON rather than α -Si₃N₄, since at this temperature Si₃N₄, if present, should be in the high temperature form, i.e. β -Si₃N₄.

Phase pure Eu- α' -SiAlON (with Eu³⁺ cations) is well known to be difficult to be synthesized, if compared to other α' -SiAlONs stabilized with other cations (e.g. Ca, Mg, Y, Yb), due to the strong tendency of europium to be in the Eu²⁺ form (cation radius 1.17 Å, too large to effectively enter inside α' -SiAlON structure) rather than in the Eu³⁺ form (cationic radius 0.95 Å) [22]. However, in the sample fired at 1700 °C, both Eu³⁺ and Eu²⁺ are believed to be present inside the α' -SiAlON lattice, as reported by Shioi et al. [23] (who effectively demonstrated, by means of XANES spectra, that Eu in the divalent state could be accompanied by a small amount of Eu in the trivalent state).

The formation of traces of Eu-containing pure nitride phase, at 1700 °C in N₂/H₂, is actually consistent with the high magnification detail in Fig. 3: the wide peak centered at about 36° could include

the peaks at 35.4° and 36.2°, corresponding to $Eu_2Si_5N_8$ [PDF#87-0423].

The likely formation of Eu- α' -SiAlON phase and Eu-doped pure nitride phase, for treatments in N₂/H₂, stimulated some preliminary tests with more conventional stabilizing cations, such as Ca²⁺, in nitrogen, considering that no previous investigation has been reported concerning the synthesis of α' -SiAlON from polymeric precursors. It can be observed that the overall amount of nano-fillers, in formulation S2 (Eq. (2)), specifically conceived for obtaining oxygen-free Eu²⁺-doped Ca- α' -SiAlON (n = 0) [6], is quite close to that for formulation S1. However, the polysilazane is the only silicon source, and no carbon excess is expected (C being removed as gaseous CO and CO₂, with conversion of oxide into nitride).

The thermal treatment at 1550 °C for 3 h in flowing nitrogen, led to the formation of Ca- α' -SiAlON, as reported in Fig. 4. The α' -SiAlON phase most compatible with the experimental pattern, according to the semi-automatic phase identification provided by the Match! program package, actually contains some oxygen, being Ca_{0.8}Si_{9.2}Al_{2.8}O_{1.2}N_{14.8} (PDF#84-0785); *n* is higher than 0 (*n* = 1.2)



Fig. 4. X-ray diffraction pattern for S2 sample heat treated in nitrogen (1550 °C, 3 h).

and m much lower than 3 (m = 1.6). As occurred for samples of formulation S1 (see Fig. 3), additional nitride phases formed, with strong peaks associated to hexagonal AlN (PDF#76–0566) and calcium silicon nitride (CaSiN₂, PDF#20-0230). Weaker peaks are compatible with β -Si₃N₄ (PDF#82-0707).

For S2 formulation, C is considered to have been almost completely removed, owing to the formation of nitride phases and to the light yellow color of the ceramic powders, typical for Eu^{2+} doped α' -SiAlON. The presence of additional phases could be due to incomplete reaction as a consequence of insufficient interdiffusion of components; part of CaO (from CaCO₃) likely reacted directly with the polymer-derived matrix, to form CaSiN₂, leaving a part of Al₂O₃ to react later, then forming AlN. Longer treatments at 1550 °C, or higher temperatures, would probably favor a closer matching of crystal phases to the expected α' -SiAlON. It is interesting to note that Eu may be incorporated in all of the crystal phases developed, resulting in efficient phosphors [24,25].

For the S2 sample, excitation was at maximum in the UV (about 300 nm) and visible (about 400 nm) regions, as illustrated by the spectrum reported in Fig. 5. The first emission peak centered at 430 nm (only observed for an excitation wavelength of about 300 nm) is attributable to emission phenomena of Eu-doped AlN in which Eu²⁺ is charge compensated by O²⁻/N³⁻ replacement or Si⁴⁺/Al³⁺ replacement. As reported in the literature [24,26], the emission peak changes its position, from 400 nm, for undoped AlN (UV emission ascribed to radiative recombination processes, involving oxygen related impurity and Al vacancies) [27], up to 460-475 nm, depending on both Eu and Si concentration. The second emission peak centered at about 570 nm (related to the excitation peak at about 400 nm) is consistent with the presence of a Ca- α' -phase doped with Eu²⁺ [6]. Apart from direct excitation of $Ca-\alpha'$ -SiAlON:Eu²⁺ for an excitation wavelength of about 300 nm, the emission spectrum indicates energy transfer from AlN:Eu²⁺ to the Ca- α' -SiAlON:Eu²⁺.

As in the case of samples of formulation S1, further refined studies on the distribution of Eu ions within the various nitride or oxynitride phases as well as the residual amorphous matrix are needed to clarify and interpret the luminescence characteristics of the developed materials in more detail. These studies will be the object of future investigation.

The present work highlights the promising potentialities of the approach of fabricating phosphor materials via preceramic polymers containing nano-sized fillers. Firstly, the processing temperatures here adopted were sensibly lower than those commonly used in the synthesis of SiAlON phosphors [6–8,28]. Secondly, a relatively wide range of commercially available polysilazanes, each providing a ceramic residue with a different balance among Si, C, N and O, could be tested, therefore possibly further extending the range of compositions, crystalline phase assemblages and emission colors obtainable.



Fig. 5. Luminescence spectra for S2 sample heat treated in nitrogen (1550 °C, 3 h): the arrows in the excitation spectrum indicate the monitoring wavelengths used for emission spectra.

4. Conclusions

We may conclude that:

- Eu-doped β' -SiAlON can be obtained from a mixture of a commercially available polysilazane and nano-sized fillers, at low firing temperature and short firing time (e.g. firing at 3 h at 1600 °C in N₂, or 1 h at 1500–1700 °C in N₂/H₂).
- Polymer-derived, phase-pure Eu-doped β'-SiAlON (with low *z*value) exhibits the expected green luminescence under blue excitation, although questions remain concerning the exact local coordination of Eu²⁺ ions in the material (only in the SiAlON lattice or also in an amorphous grain boundary phase) and the presence of more than one β' -phase. The phase formation and distribution of Eu are affected by the firing atmosphere, with SiAlON ceramics processed in N₂/H₂ displaying unusual blue and yellow emission, under near UV excitation, related to high z values of the β -phase and the presence of α -phase.
- Although not phase pure, α' -SiAlON was prepared for the first time from preceramic polymers and fillers; more precisely, Eu-doped Ca- α' -SiAlON showing its distinctive yellow luminescence, was produced.

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