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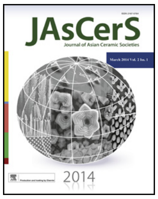

Novel synthesis of Eu-doped SiAlON luminescent materials from a preceramic polymer and nano-sized fillers

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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-Al_2O_3 and Si_3N_4 nanoparticles, whereas the Ca α-phase was achieved by adding γ-Al_2O_3 and $CaCO_3$ nanoparticles. Rare-earth ions were provided by Eu_2O_3 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).

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 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

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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_2O_3 nanopowders, 13 nm	Evonik Industries AG, Essen, Germany	5.9	17.3
Amorphous Si_3N_4 nanopowders, 20 nm	Goodfellows, Huntingdon, UK	28.4	–
$CaCO_3$ nanopowders, 90 nm	PlasmaChem GmbH, Berlin, Germany	–	16.7
Eu_2O_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-Al_2O_3 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 nano-sized 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 N_2 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 N_2 (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, N_2 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% N_2–5% H_2); in this case the cured polymer mixture was first pre-pyrolyzed at 600 °C in flowing N_2 and then fired for 1 h in the 1500–1700 °C temperature range in N_2–H_2 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 CuKα 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 μm 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:

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

$$9SiC_{0.66}N_{0.6}O_{0.03} + 1.47CaO + 1.5Al_2O_3 + 0.015Eu_2O_3 + 5.3N_2 \rightarrow Ca_{1.47}Eu_{0.03}Si_9Al_3N_{16} + 5.9CO + 0.02O_{2[excess]} \quad (2)$$

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 Al_2O_3 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