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# Yttrium silicate and oxonitridosilicate luminescent materials from a silicone resin and nano-sized fillers

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### ABSTRACT

Yttrium silicate and oxonitridosilicate ceramic powders have been successfully prepared by heat treatment, at 1300–1400 °C, of a silicone resin embedding Y<sub>2</sub>O<sub>3</sub> nano-sized particles as reactive fillers. Nano-sized RE-oxides (Eu<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>), used as secondary additives, promoted the development of apatite phase, in both air and N<sub>2</sub> atmosphere. For treatments in nitrogen, the only crystal phase consisted of yttrium nitrogen apatite, mixed with amorphous silicon oxycarbide (SiOC). Eu-doped and Ce-doped yttrium silicates were characterized by means of UV-visible luminescence and ion beam induced luminescence (IBIL). Strong luminescence features were observed, depending on the conditions of thermal treatment.

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### 1. Introduction

Silicone resins, filled with micro- or nano-sized oxide particles, have been recently introduced as precursors for many types of advanced silicate ceramics [1,2]. Besides evident shaping advantages (silicones may be easily shaped using plastic forming technologies, before ceramic conversion), this novel method allows for very favorable reaction kinetics and significant phase purity of the final ceramics. In fact, a highly reactive network of amorphous silica is formed from the oxidative decomposition of the resins and the starting materials can achieve a quasi-molecular homogeneity, considering that silicones are easily dissolved in common solvents (such as acetone or isopropyl alcohol) and nano-sized oxide particles are easily suspended in silicone solutions.

The present paper aims at evidencing the potential of silicones for the preparation of luminescent powders, for applications in modern LED devices, object of limited preliminary studies [2–4]. In particular, this work is focused on Eu- and Ce-doped yttrium silicate and oxonitridosilicate (Y–Si–O–N) ceramics with apatite crystal structure. The formation of an oxynitride phase exploits the peculiar chemistry of the ceramic residue of silicones when treated in nitrogen. In this atmosphere the ceramic residue of silicones

\* Corresponding author. *E-mail address:* enrico.bernardo@unipd.it (E. Bernardo). turns from amorphous silica to a silicon oxycarbide (SiOC) amorphous ceramic, known to feature nano-sized graphene-like carbon structures embedded in a silica glass network [5]. The following nitridation and reduction of RE ions are associated to the removal of oxygen in form of CO gas, as previously shown (at higher temperatures) for polymer-derived SiAlON ceramics [1].

## 2. Experimental

A commercially available silicone powder, MK (Wacker-Chemie GmbH, Munich, Germany) was used as silica source. The polymer was first dissolved in isopropanol and then mixed with nano-sized oxide fillers, in form of  $Y_2O_3$  (Inframat Advanced Materials LLC, Manchester, CT, USA, 30–50 nm), Eu<sub>2</sub>O<sub>3</sub> (Cometox, Milan, Italy, 45–58 nm) and CeO<sub>2</sub> (MkNano, Mississauga, Canada, 25 nm). The mixing was performed under magnetic stirring, followed by ultrasonication for 10 min, which allowed the preparation of stable and homogeneous dispersions, later cast in large glass containers and left to dry overnight at 80 °C.

After the evaporation of the solvent, the obtained silicone-based nano-composites were first finely ground with mortar and pestle, to a size of about 100  $\mu$ m, then put on alumina trays and subjected to thermal treatment in air or in flowing N<sub>2</sub> (99.99% pure) for 1 h in the 1300–1400 °C temperature range, with a 10 °C/min heating and cooling rate (in conventional muffle furnace, for treatments in air, or in alumina tube furnace, for treatments in N<sub>2</sub>).





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The crystalline phase identification was performed by means of X-ray diffraction (XRD; Bruker AXS D8 Advance, Bruker, Germany, operating with Cu K $\alpha$  radiation with the wavelength of 1.5418 Å), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA) and Match! program package (Crystal Impact GbR, Bonn, Germany).

Luminescence spectra, from ceramic powders ground and sieved to a maximum diameter of 2  $\mu$ m, were collected with a Jasco FP-6300 spectrofluorimeter, equipped with a 150 W Xe lamp. The powders were stuck on a graphite bi-adhesive scotch tape (not exhibiting any luminescence feature under UV excitation). In emission spectra the wavelength bandwidth was 5 nm for Ce containing samples and 2.5 nm for Eu doped samples.

Ion beam induced luminescence (IBIL) spectra were obtained by irradiating the powders with a 2.0 MeV H<sup>+</sup> ion beam at AN2000 accelerator of INFN Laboratori Nazionali di Legnaro (Italy). The beam current and cross section were around 40 nA and 1 mm, respectively. The luminescence spectrum was collected by a 600  $\mu$ m silica fiber and processed by an optical spectrometer (Ocean Optics QE65000-FL). Both fluorescence and UV spectra were not corrected for the spectral response of the detection systems.

#### 3. Results and discussion

In a previous work both yttrium mono-silicate (Y-MS,  $Y_2SiO_5$ , or  $Y_2O_3 \cdot SiO_2$ ) and yttrium di-silicate (Y-DS,  $Y_2Si_2O_7$ , or  $Y_2O_3 \cdot 2SiO_2$ ) from MK resin filled with  $Y_2O_3$  nano-particles, had been obtained [3]. Both silicates had been developed in conditions of good phase purity, and the doping with  $Eu^{3+}$  ions (replacing  $Y^{3+}$  ones) had been explored, only in the case of Y-mono-silicate, for the development of red phosphors.

In the present investigation Y-DS doped with 5 mol% Eu was obtained by firing at 1300 °C in air. Taking into account the silica yield of MK in oxidative atmosphere (84% [1]), the applied weight proportions,  $MK/Y_2O_3/Eu_2O_3 = 1/1.5/0.15$ , correspond to the molecular balance:

 $(MK + Y_2O_3 + Eu_2O_3)_{air} \rightarrow 0.95Y_2O_3 + 0.05Eu_2O_3 + 2SiO_2$ 

Eu-doped Y-DS is therefore formed due to the reaction:

 $0.95Y_2O_3 + 0.05Eu_2O_3 + 2SiO_2 \rightarrow Y_{1.9}Eu_{0.1}Si_2O_7$ 

For comparison, a formulation without europium (components in the weight proportion  $MK/Y_2O_3 = 1/1.6$ ) was prepared, in analogy with previous investigations.

Fig. 1 confirms the feasibility, without doping, of pure  $\alpha$ -Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> [PDF#21-1457] phase. This phase, synthesized by means of sol–gel method, has been already exploited as a host for rare-earth ions (although less effective, in terms of obtained luminescence, than  $\beta$ -phase) [6]. However, in the present synthesis procedure, the addition of Eu<sub>2</sub>O<sub>3</sub> led to the formation of an additional phase, as shown in Fig. 1. In fact, some diffraction peaks well match with yttrium silicate apatite, Y<sub>4.67</sub>(SiO<sub>4</sub>)<sub>3</sub>O [PDF#30-1457]. The development of this phase ("O-apatite") is attributed to the specific stabilizing action of Eu<sup>3+</sup> ions, in agreement with previous experiments by Cannas et al. [7] concerning sol–gel derived Y-MS ceramics: the RE dopant was found to enter preferentially into the X2-phase Y-MS and apatite, rather than in Y-DS.

The formation of yttrium silicate apatite  $(Y_{4.67}(SiO_4)_3O$ , that could be rewritten as  $7Y_2O_3$ ·9SiO<sub>2</sub>), instead of Y-DS, implies deficiency of silica in the crystalline phases, reasonably compensated by the formation of a silica-rich glass phase.

Fig. 2 reports the excitation and emission spectra of Eu-doped Y silicate powders, fired in air. A remarkable excitation peak was observed in the UV range, at 260 nm, related to the charge transfer



Fig. 1. Comparison of un-doped, Eu-doped and Ce-doped Y-DS ceramics, fired at 1300  $^{\circ}\mathrm{C}$  in air.



Fig. 2. Excitation-emission spectra of Eu-doped Y-DS ceramics.

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