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Gehlenite:Eu^{3+} phosphors from a silicone resin and nano-sized fillers

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ABSTRACT

Gehlenite ($Ca_2Al_2SiO_7$) ceramics have been successfully prepared by a novel approach, consisting of the heat treatment of a silicone resin embedding CaO and Al_2O_3 precursors, in the form of nano-sized particles that act as reactive fillers. Luminescence was due to the use of nano-sized Eu_2O_3 as secondary additive, particularly adopting a charge compensation formulation, i.e. $Ca_{2-2x}Eu_{2x}Al(Al_{1+2x}Si_{1-2x}O_7)$, with $x = 0.07$. The phase development and the emission characteristics could be adjusted by simply changing the thermal treatment applied to powders of silicone/fillers mixtures. While conventional firing at 1300 °C (for 1 h) led to practically phase-pure crystalline Eu-doped gehlenite, exhibiting a strong red luminescence, flame synthesis yielded amorphous powders, exhibiting an emission in a much broader range. When excited at 394 nm both gehlenite glass and polycrystalline gehlenite emitted light, which CIE chromaticity coordinates were found to be ($x = 0.65$, $y = 0.35$), indicating that both systems are good candidates for red light emitting phosphors.

1. Introduction

Recent investigations have demonstrated the feasibility of many types of silicate ceramics by a novel approach, based on silicone resins, filled with micro- or nano-sized oxide particles [1]. According to this method, the fillers directly react with the amorphous silica provided by oxidative decomposition of the resins, possessing a particularly defective network and consequently prone to very favorable reaction kinetics as shown, in particular, for the case of mullite ceramics (energy of nucleation below 700 kJ/mol, mullite yield above 80% after 100 s at 1350 °C) [2]. A distinctive feature of silicones, as preceramic polymers, is the possibility to shape components in the polymeric form using plastic forming technologies, before ceramic conversion; applied to silicones embedding CaO precursors (mainly $CaCO_3$) this concept has already led to several examples of cellular silicates ceramics, including 3D scaffolds [3]. However, it must be underlined that the approach is advantageous even for the preparation of un-shaped silicates, owing to the very homogeneous mixing of the starting materials: a silicone resin, in fact, is easily dissolved in common solvents such as acetone or isopropyl alcohol, and nano-sized oxide particles are easily suspended in silicone solutions. The solid residue, after solvent evaporation, can be ceramized directly in powder form, or in film form, when silicone suspensions are used as coating media. A first example, recently presented, is that of yttrium silicates from a silicone mixed with yttria nano-particles, applied as coatings for SiC components or as powders [4]; in particular, the partial replacement of Y^{3+} ions with Eu^{3+} ions, due to the use of Eu_2O_3 as secondary nano-sized oxide filler, led to luminescent powders, to be employed for LED applications.

The present paper aims at exploring the potential of nano-filled silicones for the preparation of luminescent powders based on gehlenite ($Ca_2Al_2SiO_7$ or $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$). This phase belongs to a more complex system and implies the introduction, in a silicone polymer, of more than one main oxide fillers, i.e. both CaO and Al_2O_3 precursors. If, on one hand, the possible interaction between fillers may complicate the reaction with polymer-derived silica (as recently found for cordierite, $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$, in which the formation of Mg–Al spinel, $MgO{\cdot}Al_2O_3$, was found to precede the development of the desired alumino-silicate [5]), the chosen phase, on the other, is known for its flexibility, that could promote the ionic interdiffusion. In fact, gehlenite is well-known to form solid solutions with other phases sharing its melilite-type crystal structure, such as akermanite ($Ca_2MgSi_2O_7$): 2 Al^{3+} ions in tetrahedral coordination, as an example, may be exchanged with a Mg^{2+}/Si^{4+} couple ($Ca_2Al^{3+}(Al^{3+}, Si^{4+})O_7$ turns into $Ca_2Mg^{2+}(Si^{4+}, Si^{4+})O_7$) [6].

Melilites have been increasingly considered as reference phases for luminescent materials [7–12], based on the introduction of rare-earth ions in the relatively large octahedral sites (sandwiched between layers of interconnected coordination

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tetrahedra, e.g. $Al_2SiO_7^{4-}$ for gehlenite or $MgSi_2O_7^{4-}$ for akermanite) normally occupied by Ca^{2+} ions. The polymer approach, here presented, is intended to provide an easy way for extensive industrial production, with the help of conventional firing or un-conventional treatments, such as flame synthesis, the latter representing feasible and low-cost method for preparation of a wide range of various materials. The method is based on feeding a solid (polycrystalline or amorphous) powder precursor directly into high temperature H_2/O_2 or CH_4/O_2 flame. The powder particles melt and the molten droplets are quenched by spraying them with deionized water, forming microspheres of desired composition. According to this method, high cooling rates (up to 1000 K s^{-1}) can be achieved, and even systems with high melting temperature and high tendency to crystallization can be prepared in glassy state. The method was successfully applied for the preparation of hardly meltable rare earth aluminates such as Al_2O_3–Y_2O_3 [13], [14], Al_2O_3–La_2O_3 [13,15], Al_2O_3–Gd_2O_3 [13], aluminozirconates Al_2O_3–La_2O_3–ZrO_2, Al_2O_3–Gd_2O_3–ZrO_2, Al_2O_3–Y_2O_3–ZrO_2 [13], and aluminosilicates (e.g.), Al_2O_3–Y_2O_3–SiO_2 [16]. Such amorphous structures can contain much higher level of homogeneously distributed optically active dopants, in comparison to their single crystal, or polycrystalline counterparts, representing promising laser materials or phosphors for energy saving lighting appliances. Luminescent properties of Er^{3+} and Nd^{3+}-doped amorphous yttrium aluminosicates have been reported [16].

The present work reports on a novel approach in preparation of glasses with gehlenite matrix, doped with an optically active additive (Eu). The method combines the preparation of a precursor powder from nano-filled silicones, with the application of flame synthesis to glasses of gehlenite composition. The glasses are characterized from the point of view of their luminescence properties and compared to their polycrystalline counterparts.

2. Materials and methods

2.1. Materials

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 fillers, in amounts corresponding to stoichiometric gehlenite. CaO was provided by $CaCO_3$ nano-particles (PlasmaChem, Berlin, Germany, 90 nm), whereas Al_2O_3 came from γ-Al_2O_3 nano-particles (Evonik Industries AG, Essen, Germany, 13 nm). Given the silica yield of MK (84 wt%) and the CaO yield of $CaCO_3$ (56 wt%), we referred to the silicone /Al_2O_3/$CaCO_3$ weight proportion of 1/1.43/1.57. For the preparation of luminescent powders, Ca^{2+} ions were partially replaced by Eu^{3+} ions, provided by Eu_2O_3 nano-particles (purity >99.9%, diameter 45–58 nm, Cometox Srl, Milan, Italy), for an amount of 7 mol%; the adjustment of the Al/Si ratio, necessary for charge compensation, gave the final composition of $Ca_{1.86}Eu_{0.14}Al(Al_{1.14}Si_{0.86}O_7)$ instead of $Ca_2Al_2SiO_7$ [12].

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.

2.2. Conventional and unconventional firing

After the evaporation of the solvent, the material obtained was first finely ground with mortar and pestle, to a size of about 100 μm, then put on alumina trays and subjected to thermal treatment in air ("conventional firing"), with target temperatures varying from 1100 to 1300 °C, with holding time of 1–3 h and heating rate of 10 °C/min. As an alternative (tested for Eu-doped composition), fine powders of silicone/filler mixture were sprayed into a modified glass-melting burner with methane–oxygen flame ("unconventional firing"). In order to avoid undercooling of the flame methane was used as a carrier gas. The temperature of the flame was estimated on the basis of the ability to melt the glass with the melting temperature exceeding 1900 °C, as determined from the phase diagram. The temperature in the center of the flame was thus estimated to be approx. 2200 °C. The powders were sprayed axially through the center of the burner. After passing the hot zone of the flame the stream of combustion gases carrying molten droplets was sprayed with deionized water in order to ensure rapid cooling of the product and to prevent its crystallization. The product was collected in a sedimentation vessel, and after sedimentation water was drained out. The sediment was thoroughly rinsed with acetone and dried.

2.3. Characterization

The crystalline phase identification in powders from conventional firing was performed by means of X-ray diffraction (XRD; Bruker AXS D8 Advance, Bruker, Germany, operating with Cu Kα 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).

The product of flame synthesis, in the form of microspheres with diameters ranging from 1 to approx 40 μm, was first examined by optical microscope to make sure that the input powder was thoroughly melted and glass microspheres were formed. The amorphous nature of the product was verified by X-ray powder diffraction (Panalytical Empyrean equipped with the PixCEL® detector, and with Cu Kα radiation with the wavelength of 1.5405 Å).

The density of microspheres was determined by helium pycnometry (Quantachrome Ultrapyc 1200e). The morphology of amorphous microspheres has been examined by scanning electron microscopy (JEOL 7600 F) at the accelerating voltage 15 kV. Before the measurement the microspheres were dried in laboratory oven for 24 h at 50 °C, mixed with isopropanol, and the suspension was deposited on sample holder. After drying the microspheres were sputtered with gold in order to prevent charging of the surface during measurement.

Preliminary optical characterization was conducted by means of a spectrofluorometer (FP-6300, JASCO Ltd., Great Dunmow, UK), on powders of crystalline gehlenite ground and sieved to a maximum diameter of 2 μm, dispersed in distilled water. More refined studies on both crystalline and amorphous Eu-doped gehlenite were conducted by UV–VIS–NIR spectrometry with the use of the instrument Cary 5000 (Agilent Technologies), equipped with external DRA (diffuse reflectance accessory). The instrument was used to measure reflection (absorption) spectra of prepared powder samples in the range of 200–2400 nm. The photoluminescence spectra were recorded by Fluorolog FL3-21 spectrometer (Horiba Jobin Yvon) using Xe (450 W) arc lamp as an excitation source. All the presented photoluminescence spectra have been corrected for the instrument response. The excited state lifetime was measured on the same instrument using a Xe flash lamp.

3. Results and discussion

3.1. Synthesis of Eu-doped gehlenite ceramic

The high reactivity of preceramic polymers mixed with nano-sized oxide powders is confirmed by the X-ray diffraction patterns in Fig. 1a. The $CaCO_3$/Al_2O_3/silicone mixture transformed into gehlenite (PDF#74-1607) even at only 1100 °C, for 1 h; the polymer