

# Facile obtainment of luminescent glass-ceramics by direct firing of a preceramic polymer and oxide fillers

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## ABSTRACT

Rare-earth (RE) doped glass-ceramics represent very interesting luminescent materials. The thermal annealing of the glass precursor causes the controlled precipitation of several crystalline phases, in which RE may be variously distributed, also with different oxidation states, e.g.  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ . The present investigation demonstrates the feasibility of preparation of RE-doped alumino-boro-silicate glass-ceramics by direct firing in air (at 1000–1200 °C) of a preceramic polymer, filled with nano- and micro-sized particles, as an alternative to glass melting and annealing. In particular  $\text{BaCO}_3$  or  $\text{SrCO}_3$  micro-particles, mixed with nano-sized  $\gamma\text{-Al}_2\text{O}_3$ , were found to react with amorphous silica, available from the oxidative decomposition of a commercial silicone, yielding a strontium or a barium alumino-silicate phase. Boric acid micro-particles contributed both to the development of a liquid phase upon firing (promoting ionic interdiffusion) and to the formation of a La-borate phase, by interaction with  $\text{La}_2\text{O}_3$  micro-particles. The blue and red luminescence of the obtained glass-ceramics is attributed to the incorporation of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions, from nano-sized  $\text{Eu}_2\text{O}_3$  filler, in alumino-silicate and borate phases, respectively.

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## 1. Introduction

Rare-earth (RE) ions have been widely studied over the last few decades, due to the distinctive optical properties of the materials in which they are inserted as dopants. The main applications are in solid state lighting, sensors, lasers, displays, optical amplifiers, etc [1]. Among the different RE elements, europium (Eu) has been extensively used in phosphors, in different oxidation states. The electronic configuration of Eu is  $[\text{Xe}] 4f^7 5d^0 6s^2$ , so that there are possibilities of transitions from D and F shells [2]. When incorporated in oxide matrices as divalent or trivalent ions, it is responsible for red ( $\text{Eu}^{3+}$ ) or bluish ( $\text{Eu}^{2+}$ ) photoemission. Exploiting coexisting emissions of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ , tunable phosphors can be obtained.

It is well known that, in the case of  $\text{Eu}^{2+}$ , the emission generally originates from the transition  $4f^6 5d \rightarrow 4f^7$ , typically exhibiting broad bands and being strongly field-dependent. The emission of  $\text{Eu}^{3+}$  ions, instead, shows a series of narrow bands, corresponding to  $^5\text{D}_0 \rightarrow \text{F}_{0-4}$  transitions, which are nearly independent of ligand field strength [3–5].

As reported in a recent paper by Gao et al. [6], a mixed-valence Eu-doped silicate glass-ceramic can be achieved by annealing at

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800–950 °C an alumino-boro-silicate glass (SABBL), in turns obtained by conventional melting of specific reagents at 1600 °C. This procedure, summarized in Fig. 1, led to the crystallization of hexacelsian ( $\text{BaAl}_2\text{Si}_2\text{O}_8$ ) and lanthanum orthoborate ( $\text{LaBO}_3$ ).  $\text{La}^{3+}$  sites in  $\text{LaBO}_3$  crystallites are known to host  $\text{Eu}^{3+}$  ions, whereas the  $\text{Ba}^{2+}$  sites, in hexacelsian (barium feldspar), can incorporate  $\text{Eu}^{2+}$  ions, allowing simultaneous photoemission from  $\text{Eu}^{2+}$  (bluish) as well as  $\text{Eu}^{3+}$  centers (red).

In this study, an alternative approach is proposed in order to obtain alumino-boro-silicate glass-ceramics, with final phase assemblage (comprising distribution of Eu ions) resembling that of SABBL, starting from a preceramic polymer incorporating micro- and nano-sized reactive fillers. This methodology, again schematized in Fig. 1, only requires a direct reaction at 1000–1200 °C of the ceramic precursors, thanks to the high reactivity of this system, consisting of a silicone polymer and several inorganic fillers. Indeed the fillers directly react with the amorphous silica provided by oxidative decomposition of the silicone, which exhibits a particularly defective network, being consequently prone to very favorable reaction kinetics [7]. The use of boric acid ( $\text{B}(\text{OH})_3$ ), as one of the fillers, is aimed at forming a borate liquid phase upon firing, in turn enhancing the interdiffusion phenomena. This has been already shown for the development of polymer-derived wollastonite-diopside glass-ceramics, to be applied as biomaterials, with a small amount of borax (sodium borate) among fillers [8]. In the present case, however, the boron compound is not intended to

represent simply a flux, providing a liquid phase later remaining as intergranular glass phase, after cooling; it is specifically designed to react with lanthanum oxide ( $\text{La}_2\text{O}_3$ ), leading to  $\text{LaBO}_3$ , besides its participation in the surrounding glass matrix.

The flexibility of the polymer-based approach was assessed, on a preliminary basis, by developing glass-ceramics with modified composition, owing to the replacement of  $\text{Ba}^{2+}$  with  $\text{Sr}^{2+}$  ions (SABSL). The luminescence characteristics of the SASBL glass-ceramics support the hypothesis of Eu ions distributed in a feldspar phase (Sr-hexacelsian), as  $\text{Eu}^{2+}$ , and in La borate, as  $\text{Eu}^{3+}$ .

## 2. Experimental

### 2.1. Materials and methods

A commercial silicone resin, MK (Wacker-Chemie GmbH, Munich, Germany), solid at room temperature, was considered as the silica source, with a yield of 84 wt% [7]. The polymer was added with fillers, provided in form of nano- or micro-sized particle:  $\gamma\text{-Al}_2\text{O}_3$  (Evonik Ind. AG, Germany, 13 nm),  $\text{Eu}_2\text{O}_3$  (Cometox, Italy, < 60 nm),  $\text{B}(\text{OH})_3$  (micro-sized, VWR Normapur Int.),  $\text{BaCO}_3$  (micro-sized, Sigma-Aldrich Chem., MO, USA),  $\text{SrCO}_3$  (micro-sized, Bitossi, Italy),  $\text{La}_2\text{O}_3$  (micro-sized, Sigma-Aldrich Chem., MO, USA). Two different formulations were prepared, as reported in Table 1. SABSL samples came from a modification of the SABBL composition, obtained by replacing  $\text{BaO}$  with  $\text{SrO}$ .

MK was first dissolved in isopropanol (20 ml for 10 g of final ceramic) and then mixed with the fillers. The mixing was performed by casting calibrated amounts of each filler in the solution of MK under magnetic stirring, followed by sonication for 10 min, thus obtaining stable and homogeneous dispersions. The mixtures were poured into large PTFE containers and dried at 60 °C overnight.

After drying, the silicone-based mixtures were in the form of solid fragments, later converted into fine powders by manual

grinding with pestle and mortar. The powders were cold pressed in a cylindrical steel die applying a pressure of 40 MPa for 40 s, without any additive. Disk specimens with diameter of 13 mm in diameter and approximately 3–3.5 mm in thickness were obtained and later fired in air at 1000–1100–1200 °C for 2 h, with a heating rate of 5 °C/min.

### 2.2. Characterization

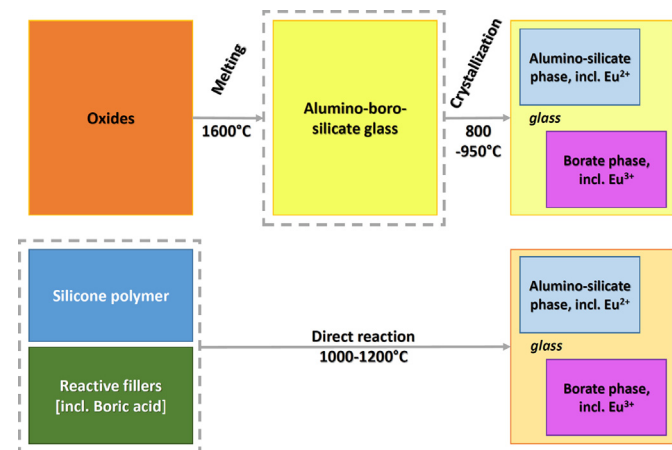
The crystalline phases were identified by means of X-ray diffraction on powdered samples (XRD; Bruker AXS D8 Advance, Bruker, Germany –  $\text{CuK}\alpha$  radiation, 0.15418 nm, 40 kV–40 mA,  $2\theta=10\text{--}70^\circ$ , step size=0.05°, 2 s counting time), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA) and Match! program package (Crystal Impact GbR, Bonn, Germany).

Photoluminescence was studied with a spectrofluorometer (FP-6300, JASCO) equipped with a Xe lamp. The emission was monitored at 612 nm and 450 nm, while the excitation wavelength was set at 250, 350, 390 nm. Luminescence spectra were collected between 280 and 800 nm.

## 3. Results and discussion

### 3.1. Phase development and evolution

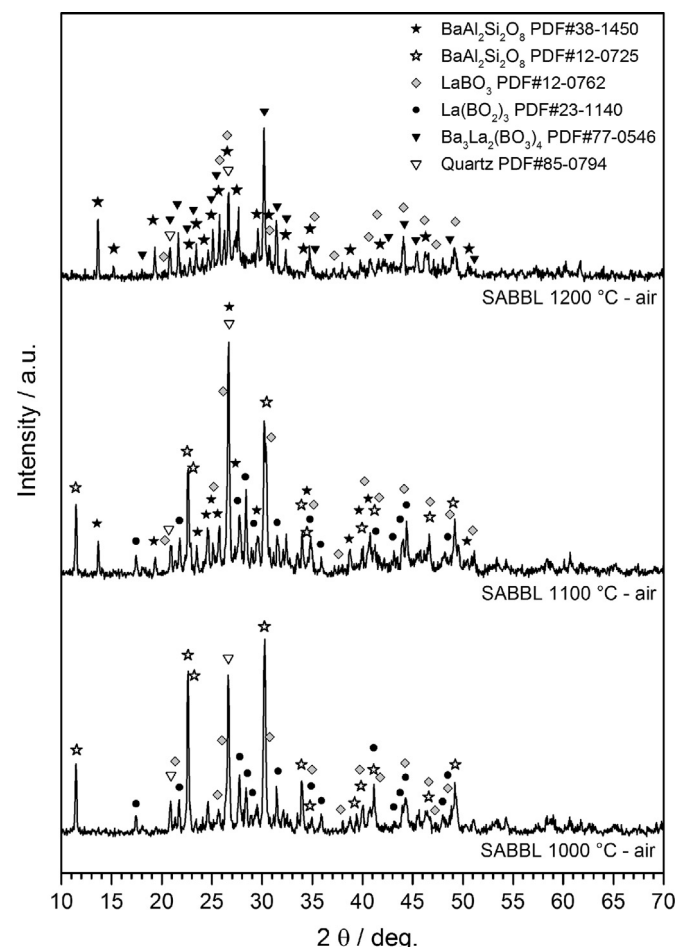
Fig. 2 reports the X-ray diffraction patterns of SABBL samples fired in air at 1000–1100–1200 °C. The lower pattern, referring to the



**Fig. 1.** Scheme for the obtention of Eu-doped glass-ceramics according to the reaction between silicones and fillers and to conventional crystallization of an aluminoboro-silicate glass (SABBL).

**Table 1**  
Nominal composition of the two ceramized samples.

Sample type	Samples composition (mol%)						
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Eu}_2\text{O}_3$	$\text{B}_2\text{O}_3$	$\text{La}_2\text{O}_3$	$\text{BaO}$	$\text{SrO}$
SABBL	33.3	10	0.2	16.7	5	35	0
SABSL	33.3	10	0.2	16.7	5	0	35



**Fig. 2.** X-ray diffraction patterns of SABBL samples fired in air at different temperatures.

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