



## Chemical tunability of europium emission in phosphate glasses

Maria Rita Cicconi<sup>a,\*</sup>, Alexander Veber<sup>a,b</sup>, Dominique de Ligny<sup>a</sup>, Jean Rocherullé<sup>c</sup>, Ronan Lebullenger<sup>c</sup>, Franck Tessier<sup>c</sup>

<sup>a</sup> Department Werkstoffwissenschaften, Lehrstuhl für Glas und Keramik, Universität Erlangen–Nürnberg, Martensstrasse 5, D-91058 Erlangen, Germany

<sup>b</sup> Energy Campus Nürnberg (EnCN), D-90429 Nürnberg, Germany

<sup>c</sup> Institut des Sciences Chimiques de Rennes (UMR CNRS 6226), équipe “Verres et Céramiques”, Université de Rennes 1, F-35042 Rennes Cedex, France

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### ABSTRACT

In this study the correlation between bulk chemistry and optical properties for a set of Eu-bearing phosphate glasses, containing different alkali elements, synthesized in air and under NH<sub>3</sub> flux, was investigated. The chemistry of the glass strongly influences several properties and the effects of bulk chemistry and synthesis conditions on glass structure and on thermal and optical properties are discussed.

In alkali-phosphate glasses studied by absorption and photoluminescence spectroscopy we verified that Eu<sup>2+</sup> emission band shifts toward higher wavelengths by substituting the alkali cation (Na < NaK < K). Nitridation enhances the glass stability and the synthesis approach carried out enhances the presence of reduced Eu species, producing modifications both on the position and on the broadening of Eu<sup>2+</sup> luminescence band.

The glass emission tunability is extremely related to the bulk composition and it is possible to adjust the chemistry in order to get the desired lighting in phosphate glasses.

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### 1. Introduction

Among the Rare Earth Elements (REE), europium and cerium are the only two elements presenting two stable oxidation states rather than only the trivalent one. Their luminescent properties are known to be very sensitive to the surrounding structural environment i.e. [1,2]. Previous studies on borophosphate, borosilicate, and boroaluminosilicate glasses [3–5] shown that the optical basicity of the glasses affects the Eu oxidation state (higher the optical basicity, higher is the amount of oxidized species). In turn, it is also possible to correlate the NBO/T parameter (non-bridging oxygen over tetrahedra) to the Eu redox ratio, as described for simplified and multicomponent silicate glasses [6–8].

Rare-earth-doped glasses are key materials for optical technology due to the luminescent properties of 4f<sup>n</sup> ions, thus REE are the most widely used phosphors in devices for lighting and displays, and also their use is economically and technologically important for applications in many fields (e.g. phosphors and LEDs). Especially the tunability of Eu allows designing versatile phosphors. Unfortunately, REE in nature are relatively rare since they are mainly present in trace amounts in minerals like carbonates, aluminosilicates and titanosilicates. Only phosphate minerals

easily incorporate large amount of REE [9]. Recently, particular attention is being paid to the possibility of improving the recycling process of REE-bearing compounds (from extraction, to reuse) and to a more efficient use of REE compounds [10].

Among phosphate materials, glasses are of great technological interest due to specific thermal properties like low thermal glass transition and dilatometric softening temperatures or high thermal expansion coefficients, which make them ideal as low-temperature sealing glasses [11]. However they suffer from a severe drawback which is often associated, i.e. their low chemical durability. Nevertheless, the nitridation ability of these glasses under ammonia is a suitable way to improve their chemical resistance [12]. During nitridation, both bridging (BO) and non-bridging oxygens of PO<sub>4</sub> are substituted by nitrogen ions, thus forming two new structural units, PO<sub>3</sub>N and PO<sub>2</sub>N<sub>2</sub> tetrahedra, where nitrogen atoms are either 2-fold (N<sub>d</sub> species) or 3-fold coordinated (N<sub>t</sub> species) with phosphorus atoms [13]. Careful synthetic control of the O/N ratio is thus important for tuning the materials properties of the final oxynitrides, especially when mixed oxidation states are present. Oxide and nitride may substitute for each other in many crystalline structures if a compensating redox mechanism involving cations is available [14].

Ammonolysis is a technique which presents many advantages for the synthesis of oxynitride phosphors. A typical set-up for ammonolysis only involves a tubular furnace with flowing ammonia gas. Furthermore, ammonolysis shows a decisive advantage

\* Corresponding author.

E-mail address: [maria.rita.cicconi@fau.de](mailto:maria.rita.cicconi@fau.de) (M.R. Cicconi).

for phosphor synthesis: ammonia gas is both reduced and nitrated. Indeed,  $\text{NH}_3$  is totally dissociated at the reaction temperature (see Appendix A), and since nitrogen and hydrogen produced by the decomposition of ammonia are in nascent state, they are very reactive in terms of reduction-nitridation abilities. As a consequence, nitridation is expected to lead both significant changes in NBO/BO and  $\text{Eu}^{3+}/\text{Eu}^{2+}$  redox ratio.

Europium characteristic emissions have been widely investigated in many systems, and  $\text{Eu}^{3+}$ -bearing materials are promising red-emitting solid-state materials. Indeed, most of these studies were focused on the understanding of the structural environment of  $\text{Eu}^{3+}$  ions, due to the narrow and almost monochromatic  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition at  $\sim 613$  nm and to its long lifetimes [e.g. [2,15,16]]. Nevertheless, in the past decades many studies tried to influence the valence states of europium ion in solid-state materials, mainly in borate, boro-silicate and boro-phosphate glasses, or silicate and aluminosilicate glasses [[3–5] and references therein].

In this study we investigated europium in a set of metaphosphate glasses in order to verify the effect of bulk chemistry and nitridation on both Eu redox state and optical properties.

The choice of a phosphate host composition as base composition was also guided by environmental considerations i) production of phosphate glasses requires lower synthesis temperatures, and therefore less energy, with respect to silicate glasses or ceramics; ii) REE could be reconcentrated by crystallization of phosphate phases after the use of the device in order to form congruent minerals and in turn, to recover REE; iii) crystallized REE species could be extracted by using the procedures already established for phosphate minerals in Ore deposits. REE-based device will be then a real environmental friendly product where the total life cycle would have been optimized.

Being the first part of a larger project on the development of “green” Eu-based phosphors, this work report how different phosphate glasses act on Eu redox and luminescence behaviour.

## 2. Experimental methods

Europium phosphate glasses were prepared by mixing dry europium oxide (1 wt%  $\text{Eu}_2\text{O}_3$ ) and phosphate salts ( $\text{NaPO}_3$ ,  $\text{Ca}(\text{PO}_3)_2$ ,  $\text{KPO}_3$ ) in stoichiometric proportions. The mixture was melted in a quartz crucible at  $900^\circ\text{C}$  for 30 min and glasses were obtained by pouring the melt into preheated brass molds. Annealing process was carried out at  $325\text{--}350^\circ\text{C}$  for 30 min and then the material was cooled down to room temperature in 3 h. Aliquots on the order of 1 g of each glass were melted at  $750^\circ\text{C}$  in a glassy carbon crucible under  $\text{NH}_3$ -flux for 19 h (heating rate  $10^\circ\text{C}/\text{min}$ ). This temperature avoids the phosphorous reduction, and the low viscosity of the melt at this temperature determines the

nitridation rate, which is a diffusion controlled phenomenon, and also affects the maximum nitrogen content in the glass matrix.

The batch compositions of the investigated glasses are reported in Table 1. All the samples synthesized in air appeared highly transparent and were checked for homogeneity and absence of crystals by XRD, optical microscopy and Raman. Small pieces of these glass samples were polished and used for optical measurements. N-treated samples were transparent, even if they present bubbles. Only the K sample after nitridation shown some crystallization on one side of the crucible, the non-crystallized part was used after checking that its chemical composition was not modified from the nominal one. Nitrogen analysis was carried out in a  $\text{N}_2/\text{O}_2$  analyzer LECO. The glass characteristic temperatures, i.e. glass transition, onset crystallization peak and melting, of both Eu-bearing and undoped samples were measured from differential scanning calorimetry (DSC, NETZSCH DSC 404F1) at a constant heating rate of  $10^\circ\text{C}/\text{min}$ . In all cases no aging of the samples was observed demonstrating a good behavior in regard of atmospheric water.

Analyses of optical emission and excitation behavior (PL) were performed with a spectrofluorometer equipped with double monochromators (Czerny-Turner) in excitation and emission (Fluorolog3, Horiba Jobin Yvon; used spectral resolution  $\sim 0.5$  nm), using a 450 W Xe-lamp as excitation source. Absorption spectra were measured using an UV/VIS spectrometer (Lambda 950, Perkin Elmer).

## 3. Results

### 3.1. Thermal properties

Table 1 shows different properties of the studied glass compositions. After the same heat treatment, the maximum nitrogen content is much lower for the Na-bearing glass. When potassium is substituted for sodium, or whether potassium is the only alkali element, the nitrogen content increases drastically.

Considering undoped glasses as references, it is obvious that both europium and nitrogen greatly enhance the glass transition temperature and the onset temperature of crystallization. On the contrary, the melting temperatures are decreasing. In Fig. 1 are reported the DSC curves for the three metaphosphate glasses doped with 1 wt%  $\text{Eu}_2\text{O}_3$  where it can be seen a clear variation of the glass transition ( $T_g$ ), the melting ( $T_m$ ) and the crystallization temperature ( $T_x$ ) depending on the glass chemistry. In particular, the mixed alkali effect is evidenced on  $T_g$  values (inset in Fig. 1), as for the undoped glasses. However, when nitrogen is introduced in the glass network, the mixed alkali effect disappears (Table 1). The Hruby parameter [17] is also largely increased when both europium and nitrogen are added to the based oxide glasses, providing

**Table 1**  
Compositions (mol%), optical basicity ( $\Lambda$ ) and some properties of the phosphate glasses. Eu-bearing glasses have been doped with 1 wt%  $\text{Eu}_2\text{O}_3$ .

Sample	$\text{P}_2\text{O}_5$	CaO	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	N content (wt%)	$T_g$ ( $^\circ\text{C}$ )	$T_m$ ( $^\circ\text{C}$ )	$T_x$ ( $^\circ\text{C}$ )	$(T_x - T_g)/(T_m - T_x)$ §	$\Lambda$
NaP	50	20	30	–	–	351	735	547	1.04	0.52
NaPEu	50	20	30	–	–	373	706	586	1.78	
NaPEu-N	50	20	30	–	0.86	392	678	602	2.76	
NaKP	50	20	15	15	–	320	700	565	1.81	0.53
NaKPEu	50	20	15	15	–	331	692	568	1.91	
NaKPEu-N	50	20	15	15	4.42	395	–	–	–	
KP	50	20	–	30	–	342	698	480	0.63	0.54
KPEu	50	20	–	30	–	353	680	499	0.81	
KPEu-N*	50	20	–	30	4.45	377	644	534	1.43	

$T_g$ =glass transition temperature;  $T_m$ =melting temperature;  $T_x$ =crystallization temperature.

\* Partially crystallized ( $\text{KCa}(\text{PO}_3)_3$ ); § Hruby parameter [17].

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