Influence of Y$_2$O$_3$ and Gd$_2$O$_3$ additives on luminescence properties of CaO-2SiO$_2$:Ce glasses

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Alkali-earth glasses with Y$_2$O$_3$ and Gd$_2$O$_3$ additives have been obtained using traditional melt technology. The influence of Y$_2$O$_3$ and Gd$_2$O$_3$ on photoluminescence, radioluminescence, and structural properties of investigated glasses has been investigated and discussed.

1. Introduction

Nowadays, scintillation materials are widely used in various fields, such as high-energy physics, medicine, geology, homeland safety, etc. In this regard the search and development of efficient and unexpensive scintillation materials are important and actual [1,2]. Particular attention can be paid to glasses: they are characterized by a low cost, simplicity of processing, optical transparency, easy tuning of a variety of compositions. Moreover, silicate scintillators in single crystal form like rare-earth ortho- and pyrosilicates are well known. They are characterized by a high light yield (LY) (up to 40000 ph/MeV for gadolinium pyrosilicate - GPS) and energy resolution (up to 6% for GPS) [3]. Their silicate-based composition allows to obtain similar compounds in glass or glass-ceramic form by combination with silica based glasses. The combination of rare-earth ortho- and pyrosilicates with alkali-earth silica glasses looks especially attractive in order to improve LY and reduce the afterglow [4].

Therefore, this work was focused on the preparation of calcium silica glasses with additions of Gd$_2$O$_3$ and Y$_2$O$_3$ and on the study of their photoluminescence (PL) and radioluminescence (RL) properties.
2. Materials and methods

2.1. Samples synthesis

Glass samples with compositions 3CaO-2SiO₂-Ce (from now on CaSi), (CaO-2SiO₂)0.34Y₂O₃-Ce (CaY) and (CaO-2SiO₂)0.34Gd₂O₃-Ce (CaGd) have been obtained using traditional solid-state melt technology. CaCO₃, SiO₂, Y₂O₃ or Gd₂O₃ have been used as raw materials. Raw materials in the required quantities were mixed in a mortar by grinding. CeO₂ was introduced for substitution of 1 at% of Ca²⁺ ions in the glasses. The resulting mixtures were transferred in Al₂O₃/ZrO₂ crucibles that were placed in a FALORNI gas furnace where they were annealed in reducing atmosphere at 1550 ºC for 3 hours. The glass melts were casted on steel plates and after that placed in an electrical furnace at 600 ºC for 4 hours. Finally for optical measurements, glass specimens were cut on plates with ~1 mm thickness and polished.

2.2. Samples Characterization

X-ray excited radio-luminescence (RL) measurements were carried out at room temperature with a home-made apparatus featuring a CCD detector (Jobin-Yvon Spectrum One 3000) coupled to a monochromator (Jobin-Yvon Triax 180) with a 300 grooves/mm grating. X-ray irradiations were performed by a Philips x-ray tube operating at 20 kV. All irradiation were carried out in the same conditions varying only the exposition time. Steady state PL spectra were measured at RT by a xenon lamp as excitation source, together with a double monochromator (Jobin-Yvon Gemini 180 with a 1200 grooves/mm grating), and recorded through a nitrogen cooled CCD detector coupled to a monochromator (Jobin-Yvon Micro HR). Raman measurements were performed in backscattering configuration with a frequency doubled Nd:YAG laser as excitation (wavelength λ = 532 nm) on a Jobin-Yvon T64000 triple monochromator equipped with a liquid nitrogen cooled CCD (Jobin-Yvon Symphony). The measurements detection range was 100-3500 cm⁻¹.

3. Results and Discussion

PL and RL spectra of the investigated glasses are presented in fig. 1 where a comparison with calcium silica glass is also proposed. Concerning emission spectra (fig.1a) a broad and unresolved band corresponding to the 5d₁ - ⁷F₅/₂ and 5d₁ - ⁵F₇/₂ radiative transitions of Ce³⁺ ions is observed for all samples. The spectra are characterized by a similar peak
position (405 nm) independently of the composition. CaY and CaGd are characterized by a higher PL intensity than calcium silica glass.

All samples are characterized also by a broad RL spectrum (fig. 1b). For CaGd, an additional band at 320 nm (correspond $^4\text{P}_j \rightarrow ^8\text{S}_{7/2}$ transition for Gd$^{3+}$ ions) is observed. The highest RL intensity belongs to CaGd and CaY samples and can be the result of crystalline ortho- and pyrosilicate structures formation in glasses.

The different spectral shapes between RL and PL of glasses with Gd$_2$O$_3$ and Y$_2$O$_3$ suggest the presence of Ce$^{3+}$ ions in different surroundings and/or the occurrence of defect emissions, and deserve further investigations in the future.
Raman spectroscopy was used to investigate the structure of glasses (fig. 2). Around ~1000 cm⁻¹ Raman structures are evidenced, corresponding to anti-symmetric stretching vibrations of SiO₄ tetrahedra and possibly also to vibrations of units with two non-bridging oxygens characteristic of metasilicate compositions. At lower wavenumbers, the spectra turn out to be clearly dependent on composition and will be the subject of further investigations.

4. Conclusions

In this work we have demonstrated the possibility to prepare Ce-doped silicate glasses with mixed Y- and Gd composition. We have also revealed that their optical properties depend on composition, and that PL and RL spectra are different suggesting the presence of Ce³⁺ ions in different surroundings and/or the occurrence of defect emissions in RL. Moreover, clear differences are evidenced in Raman spectra due to the structural characteristics of the investigated glasses. Future work will be devoted to a deeper insight on the optical properties of such materials in relation to their structural features.

Acknowledgments

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