Photo- and radio-luminescence properties of $3CaO\text{-}2SiO_2$ and $3CaF_2\text{-}2SiO_2$ glasses doped by Ce^{3+} ions

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Abstract

Wavelength-shifting materials in the form of optical fibers are requested in order to both convert UV scintillation light produced by fast scintillators into a more easily detectable visible light, and to efficiently transport it to the detectors.

In the present investigation we have considered glasses with composition $3CaO\text{-}2SiO_2$ and $3CaF_2\text{-}2SiO_2$ doped with 0.05, 0.5 and 1 at. % of Ce^{3+} ions, prepared by an original method consisting in a combination of co-precipitation and sol-gel approaches. The glasses have been investigated by Raman scattering, as well as by photo- and radio-luminescence.

The glasses are characterized by complex Raman features. Composite photoluminescence excitation and emission spectra are also detected in all cases, depending upon glass composition and Ce concentration. Broad excitation spectra extend from approximately 260 nm to 360 nm, while the composite Ce^{3+} emission is detected in the blue spectral region at around 400 nm. A satisfactory matching between the excitation spectra of the glasses and the emission spectrum of CeF_3 scintillator occurs, confirming their potential application as wavelength shifters of CeF_3 UV scintillation light. Moreover, bright photoluminescence signals are accompanied by a very poor radio-luminescence. The results are discussed by taking into account the presence of different silicate clusters embedded in the glass network, as well as the role of point defects in the radio-luminescence process.

Keywords: Glasses; luminescence; scintillations

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1. Introduction

A great variety of single crystals possess favorable properties as scintillators materials, like high luminescence efficiency coupled to a small amount of defects and traps that could influence the carrier recombination process. Nonetheless, crystals have also a number of disadvantages that sometimes limits their application. In fact, they often have a high cost, due to the expensive equipments for their production, slow and expensive growth. The growth of large crystals is also a challenge. The search of alternatives to single crystals for application in ionizing radiation detectors is therefore an important task [1, 2, 3, 4, 5].

Besides crystalline materials, there are a great number of other inorganic materials that can be promising scintillators, specifically, glasses. The main origin for their often poor scintillation is their disordered structure, which leads to the formation of a great number of traps, competing with luminescent ions in free carrier capture. On the other hand, glasses can be obtained with a wide variety of compositions, and moreover glass-ceramics can also be prepared thanks to a partial crystallization of the network [6, 7]. Such versatility encourages their development through controlled preparation techniques and suitable doping.

Among glassy materials, silicates look to be the most promising hosts for developing new phosphors. Silica is a glass forming compound. Moreover, silicates in the crystalline phase find numerous application as luminescent materials. Single-crystalline $(RE)_2SiO_5$ and $(RE)_2Si_2O_7$ silicates (RE = Lu, Y, Gd) doped with Ce^{3+} are good scintillating materials [8, 9, 10, 11]. Similarly to single crystals, some silicate glasses show bright near UV or blue luminescence. For example, lithium silicate glass is widely used as neutron sensitive scintillating sensors [12]. Glass and glass ceramics made of stoichiometric Li_2O-$2SiO_2$ composition possess a light yield better than 7000 ph/n [13]. Glass made of stoichiometric BaO-$2SiO_2$ composition features a high photo-luminescence quantum efficiency, scintillation light yield at the level of 1000 ph/MeV, and good hardness after irradiation with gamma rays and 150 MeV protons [7, 14]. These features make silicate stoichiometric glasses promising materials in fiber or bulk form for nuclear instrumentation. For example, silica fiber sensors doped with Ce^{3+} or Yb^{3+} ions are being investigated for real time remote dosimetry in medical diagnostic and therapy [15, 16].

Moreover, recently particular interest for glasses was raised by their application potential to act, in fiber form, as wavelength shifters (WLS) of UV scintillation light emitted for example by CeF_3 and BaF_2 [17, 18] and neutron sensitive Li-Si-Al scintillation glass emitting in a near UV range [19]. Their scope is to transform UV emitted light in a more easily detectable visible emission, and simultaneously provide its transport to the detector. At variance with other applications, in this case the material has to possess a low density and a poor scintillation yield. These features make such type WLS fibers to be not sensitive to ionizing radiation and exclude their contribution in the signals of the detecting units, which is particularly important in high energy physics experiments.

To the purpose of developing wavelength shifting materials, we considered

Table 1: Glass samples names, their compositions and Ce^{3+} ions concentrations

Short name	Composition	Ce^{3+} ions concentration, at. % of Ca^{2+} ions
CaO005	3CaO-2SiO_2	0.05
CaO05	3CaO-2SiO_2	0.5
CaO1	3CaO-2SiO_2	1
CaF005	3CaF_2-2SiO_2	0.05
CaF05	3CaF_2-2SiO_2	0.5
CaF1	3CaF_2-2SiO_2	1

glasses with 3CaO-2SiO_2 composition. Moreover, we also report the effect of partial substitution of oxygen ions by fluorine ions on luminescent properties of Ce^{3+} ions in a calcium silicate glass system with 3CaF_2-2SiO_2 composition. As described below, we used a complex method consisting in a combination of co-precipitation and sol-gel approaches, to produce glass precursors.

2. Materials and Methods

$Ce(NO_3)_3{\cdot}6H_2O$, NH_4F, TEOS, ethanol, $Ca(NO_3)_2{\cdot}4H_2O$, NH_4HCO_3 were used as starting materials. All reactants were analytical grade.

Two different kinds of glasses with different Ce^{3+} concentrations, 3CaO-2SiO_2:Ce and 3CaF_2-2SiO_2:Ce, were obtained. The main difference between glasses lies in using different calcium compounds doped by Ce^{3+} ions, obtained by co-precipitation method CaF_2:Ce for 3CaF_2-2SiO_2:Ce glasses and $CaCO_3$:Ce for 3CaO-2SiO_2:Ce glasses.

CaCO3:Ce has been obtained by co-precipitation of mixed water solution of $Ca(NO_3)_2$ and $Ce(NO_3)_3$ into water solution of NH_4HCO_3. CaF_2:Ce has been obtained by co-precipitation of mixed water solution of $Ca(NO_3)_2$ and $Ce(NO_3)_3$ into water solution of NH_4F. The quantity of $Ce(NO_3)_3$ corresponds to substitution of 0.05, 0.5 or 1 at. % of Ca^{2+} ions by Ce^{3+} ions. Isolated precipitates of $CaCO_3$:Ce and CaF_2:Ce have been introduced into water-alcohol solution of TEOS, which has then been subjected to alkaline hydrolysis. The obtained gels of precursors of 3CaO-2SiO_2:Ce and 3CaF_2-2SiO_2:Ce glasses were dried in air at 80 °. The resulting xerogels (in powder form) were melted in a Falorni gas oven in ZrO_2/Al_2O_3 crucibles at 1500 °C for 3 hours. To avoid crystallization during cooling, the glasses were casted on non-preheated steel blocks and subsequently treated in a Nabertherm LHT 18/04 muffle furnace preheated at 580 °C to reduce mechanical stresses. The obtained glass blocks were transparent and colorless. For optical measurements, specimens with thickness 1 mm were cut and polished. Samples short names and their composition are listed in Table 1.

Some comparisons were performed with a sol-gel SiO_2:0.1 mol. % Ce^{3+} ions sample sintered in reducing conditions [20], and with a CeF_3 single crystal.

X-ray excited radio-luminescence (RL) measurements were carried out with a homemade apparatus featuring a CCD detector (Jobin-Yvon Spectrum One 3000) coupled to a monochromator (Jobin-Yvon Triax 180) with a 300 grooves/mm

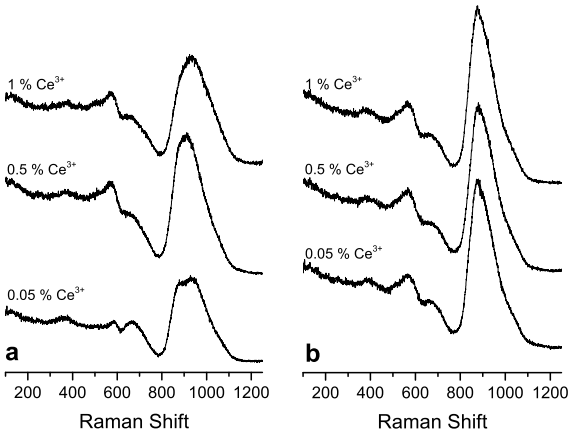

Figure 1: Raman spectra of CaO-SiO_2:Ce(a) and CaF_2-SiO_2:Ce(b) glasses

grating. RL was excited by X-ray irradiation using a Philips 2274 tube operating at 20 kV and 20 mA. All X-ray irradiations were carried out in the same conditions varying only the exposition time.

For optical absorption a Varian Cary 50 spectrophotometer was used. The optical absorption spectra were acquired in the 190-1100 nm wavelength range.

Steady state photoluminescence (PL) spectra were measured using a xenon lamp as excitation source, followed by a double monochromator (Jobin-Yvon Gemini 180 with a 1200 grooves/mm grating), and recorded by 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 source ($\lambda = 532$ 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}.

All measurements were performed at room temperature (RT).

3. Experimental Results and Discussion

The Raman spectra of alkali-earth silicate glasses are discussed in detail in [21, 22, 23, 24, 25]. In general, the Raman spectra of investigated glasses seem to be similar and their differences mainly consist in the relative intensities of the bands (Fig. 1).

The most intense signal is located between 800 and 1150 cm^{-1} and it consists of a broad unresolved and asymmetric structure featuring principal components with maxima at around 875 cm^{-1} and 910-935 cm^{-1}. The band at 875 cm^{-1} could be assigned to symmetric stretching vibrations of non-bridging oxygen

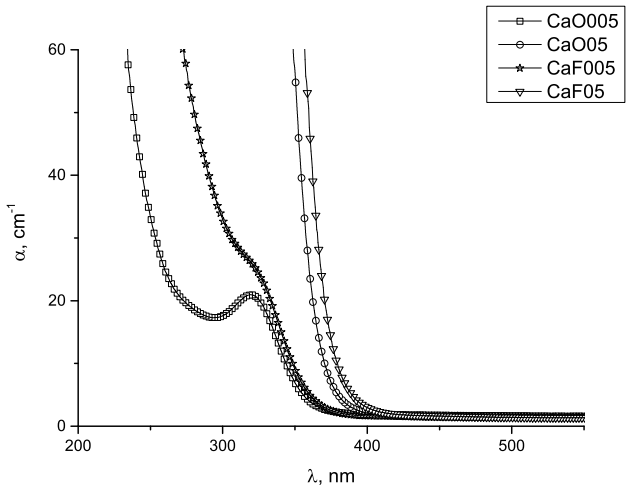

Figure 2: Optical absorption spectra of CaO005, CaO05, CaF005 and CaF05

bonds in separate SiO_4^{4-} tetrahedra in the orthosilicate structure [22]. The band with maximum at 910-935 cm^{-1}, in principle, can be associated to two kinds of vibrations. It can correspond to $Si_2O_7^{6-}$ vibrations in the pyrosilicate structure, or to the presence of $(SiO_4)n^{2-}$ chains [23, 25]. The band located above 1000 cm^{-1} (it looks like a weak shoulder in both families of samples) could correspond to the anti-symmetric stretching vibration in a three-dimensional array of SiO_4 tetrahedra [22]. The weak broad band at 650-660 cm^{-1} can be assigned to Si-O-Si linkages and asymmetric stretching vibrations of bridging oxygen bonds in crystalline pyrosilicates [22]. Moreover, the band at 575-580 cm^{-1} could correspond to bending motions of oxygen bonds in direct structures in quenched SiO_2 [25]. The broad structure located between 100 and 500 cm^{-1} contains the contribution from the rocking mode of silica at 440 cm^{-1} [25, 26, 27].

In general, substitution of O^{2-} with F^- should distort the electronic environment of silica because of the higher electronegativity of F^- compared to the O^{2-} one. This distortion could weaken the remaining Si-O bonds in the silica tetrahedron, decreasing the force constants and the vibrational frequencies involving these Si-O bonds. As a result, increasing the F^{2-}-to-O^{2-} ratio in SiO_xF_y compound is expected to decrease the frequency of the resultant bands in the Raman spectrum up to $\sim$50 cm^{-1} per oxygen replaced by F^- [28]. However in the investigated samples the Raman spectra are similar, and only relative bands intensity differences are observed. This indicates a weak influence of F^- on the glass network, possibly due to the fact that fluorine ions are predominantly coordinated near Ca^{2+} ions [21, 28].

The optical absorption spectra of CaO005, CaO05, CaF005 and CaF05 glasses are in Fig. 2.

A partially unresolved peak at 320 nm is observed for CaO005 sample. It is

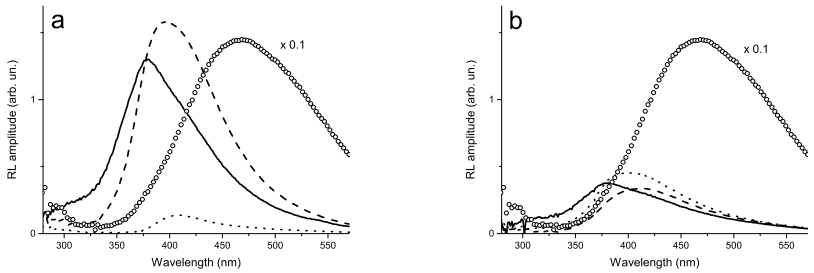

Figure 3: RL spectra of glasses with composition 3CaO-2SiO_2 (a) and 3CaF_2-2SiO_2 (b) with 0.05 (solid line), 0.5 (dashed line) and 1 (dotted line) at. % of Ce^{3+} ions in comparison with BGO (marked as circles, spectrm is multiplied by 0.1)

manifested as a shoulder for the CaF005 sample. This peak corresponds to the lowest 4f-$5d^1$ inter-configuration transition of Ce^{3+}. Increasing the concentration of Ce^{3+} ions strongly increases this absorption and only its long wavelength tail could be measured in samples with 0.5 at. % Ce (CaO05 and CaF05). In low-Ce^{3+} samples, at wavelengths below 300 nm a very strong absorption increase is detected. The origin of this absorption deserves further investigations, taking into account the role of charge compensating defects due to the presence of Ca^{2+} and F^- in the silica network.

The RL spectra of the investigated samples are presented in Fig.3.

The RL spectra shape depends on Ce^{3+} concentration. All the emissions consist of unresolved $5d^1$-$^2F_{5/2}$ and $5d^1$-$^2F_{7/2}$ radiating transitions of Ce^{3+}. For CaO005 and CaF005, the emission peak is at approximately 380 nm. Increasing the Ce^{3+} concentration leads to a red shift: up to ∼395 and ∼410 nm for CaO05 and CaF05 samples respectively, and up to ∼405 and 400 nm for CaO1 and CaF1 samples respectively. The red shift is probably related to the absorption spectra modifications displayed in Fig.2: in other words, it might be an effect of a stronger re-absorption of the short wavelength side of the luminescence emission band.

The intensity difference of the RL spectra for 3CaO-2SiO_2 and 3CaF_2-2SiO_2 samples can be explained by the difference in their anionic surrounding. Partial substitution of oxygen ions by fluorine ions can contribute to the increase of the number of defects that work as traps and lead to a decrease of the scintillation efficiency.

Photo-luminescence excitation spectra (for 420 nm emission) are presented in Fig. 4. For all 3CaO-2SiO_2 and 3CaF_2-2SiO_2 samples the spectra consist of several unresolved bands, also influenced by the Ce^{3+} content.

Excitation spectra extend from approximately 260 nm to 390 nm. A stronger contribution at wavelengths below 300 nm is detected for 3CaO-2SiO_2 with respect to 3CaF_2-2SiO_2. For 3CaO-2SiO_2:Ce glasses the long wavelength excitation part (corresponding to the 4f→$5d^1$ transition of Ce^{3+}) displays a red shift with increasing Ce^{3+} concentration from 335 nm (sample CaO005) to 355 nm

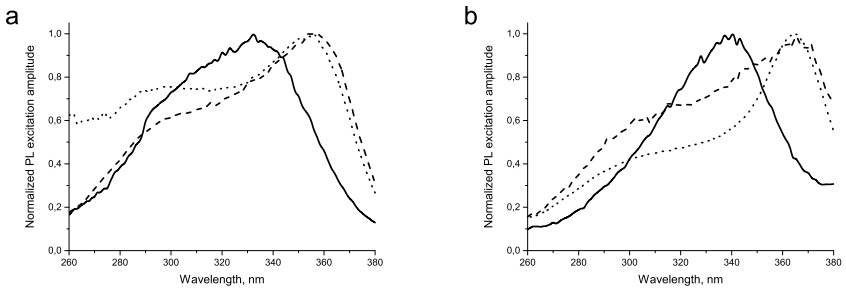

Figure 4: Normalized excitation spectra for $3CaO\text{-}2SiO_2$:Ce (a) and $3CaF_2\text{-}2SiO_2$:Ce (b) glasses with 0.05 (solid line), 0.5 (dashed line) and 1 (dotted line) at. % of Ce^{3+} ions

(samples CaO05 and CaO1). The same phenomenology is observed in $3CaF_2$-$2SiO_2$:Ce samples: the long wavelength part of the band is shifted from 340 nm (sample CaF005) to 365 nm (samples CaF05 and CaF1). This effect is most probably due to the high light absorption level while Ce^{3+} concentration is increased.

PL emission spectra at different excitation wavelengths (300 nm, and 360 nm) are reported in Fig. 5.

For both kind of glasses, remarkable spectral shifts are observed as a function of excitation wavelength and Ce^{3+} concentration. For example, under 300 nm or 360 nm excitation, the emission peak positions of CaO005 result to be 385 nm and 420 nm respectively. In general, the presence of different emission peaks can be the result of the presence of Ce^{3+} ions in different surroundings. This is also suggested by Raman data that reveal the occurrence of vibrations related to different silicate structures. With the increase of the Ce^{3+} content, part of them are localized in new different surroundings. The comparison between PL and RL spectra demonstrates that the center responsible for the emission excited at 300 nm gives a major contribution under ionizing radiation excitation. Interestingly, in two cases (Fig. 5 c, f) the RL occurs at still lower wavelengths with respect to PL, indicating the presence of a third kind of cerium center that was not evidenced in our PL experiments.

Weak RL intensities and bright PL emissions with UV excitation in a wide spectral range make these glasses interesting materials as wavelength shifters in combination with UV emitting scintillators, for example CeF_3 or Ce-doped Li-Si-Al scintillating glasses. In order to qualitatively display such characteristic, a comparison between PL and RL intensities of $3CaO\text{-}2SiO_2$ with 0.5 % Ce^{3+} and sol-gel SiO_2: 0.1 mol % Ce sintered in reducing conditions [20] is shown in Fig. 6.

The PL intensity for CaO05 is 3 times lower than that of SiO_2:Ce glass, while the RL intensity of CaO05 is lower than that of SiO_2:Ce glass by more than two orders of magnitude. Similar results occur also for the other glass compositions investigated.

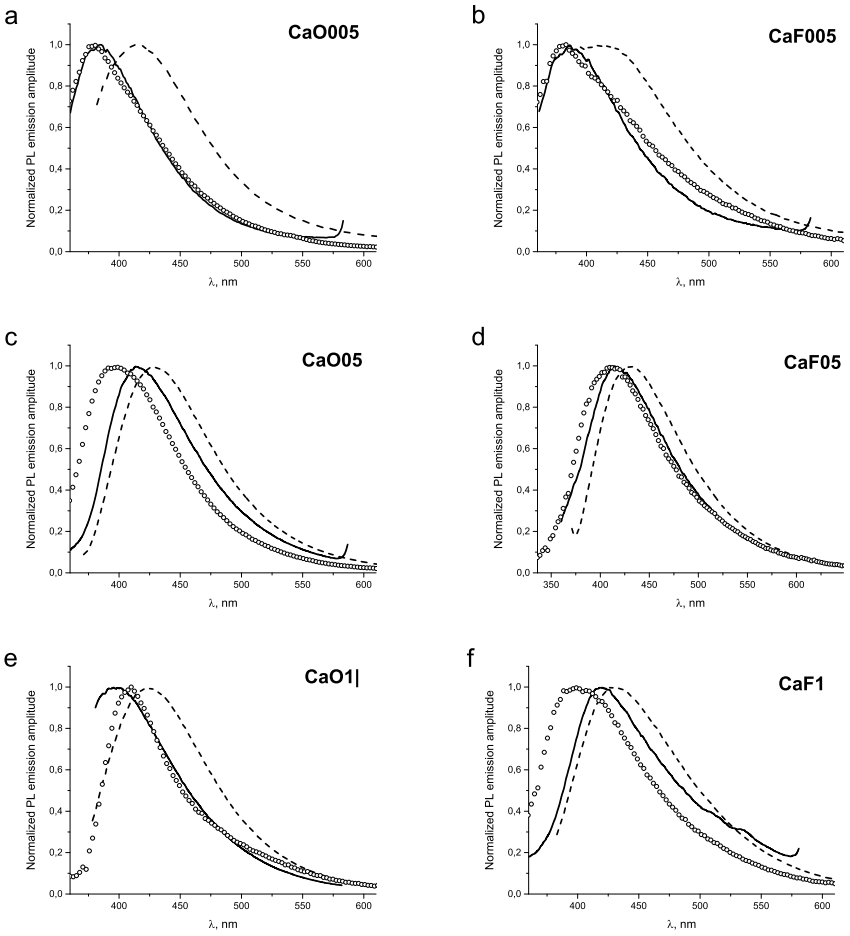

Figure 5: Normalized PL emission spectra obtained with excitation at 300 nm (solid line) and 360 nm (dashed line) for $3CaO\text{-}2SiO_2$ (a, c, e) and $3CaF_2\text{-}2SiO_2$ (b, d, f) glasses with 0.05 (a, b), 0.5 (c, d) and 1 (e, f) at. % of Ce^{3+} ions in comparison with their normalized RL spectra (marked by circles)

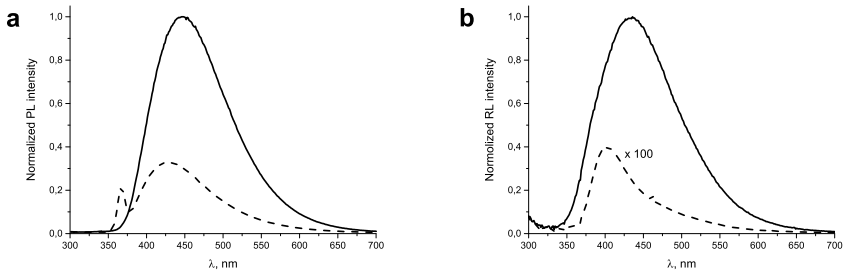

Figure 6: Comparison between PL (panel (a)) and RL (panel (b)) measurements of sol-gel SiO_2: 0.1 % Ce (solid lines) and CaO05 (dashed lines). Data are normalized with respect to sol-gel SiO_2:Ce. In panel (b) the RL curve of 3CaO-2SiO_2 glass is multiplied by 100. For PL, λex were 350 nm for SiO_2:Ce glass and 360 nm for CaO05.

Fig. 7 displays the satisfactory spectral overlap between CeF_3 RL emission and the PLE excitation bands of CaO1 respectively. Such overlap allows 3CaO-2SiO_2:Ce glass to absorb efficiently the UV light emitted by CeF_3 converting it in the blue spectral region.

4. Conclusions

3CaO-2SiO_2 and 3CaF_2-2SiO_2 glasses doped with different Ce^{3+} concentrations have been produced using an original method consisting in a combination of co-precipitation and sol-gel approaches. Their optical properties have been investigated in order to explore their potential application as wavelength shifters coupled to a UV-emitting scintillator, transforming the UV scintillation light into a more easily detectable visible emission. Moreover, fibers drawn from these materials could allow a more effective scintillation light extraction in detectors with complex geometries.

Bright and composite photoluminescence emissions around 430 nm are observed in all samples, characterized by broad excitation spectra extending from approximately 260 to 390 nm. The excitation spectra well match the emission spectrum of CeF_3 and Li-Si-Al scintillation glass; such matching proves the capability of the glasses to act as wavelength shifters thanks to their strong absorption of UV scintillation, and its conversion into a longer wavelength radiation. Moreover, very weak radio-luminescence signals are displayed by all samples. The different behaviors of the glasses during intra-center or above-band-gap excitations can be explained by taking into account the presence of defects in the glasses, affecting the transport stage of scintillation. This results in a different involvement of the host matrix during the two kinds of experiments. In fact, during irradiation with ionizing radiation the free carriers experience a significant migration in the host prior to be localized at luminescent centers (Ce^{3+} in our case). During such migration path, they can be trapped by defects which

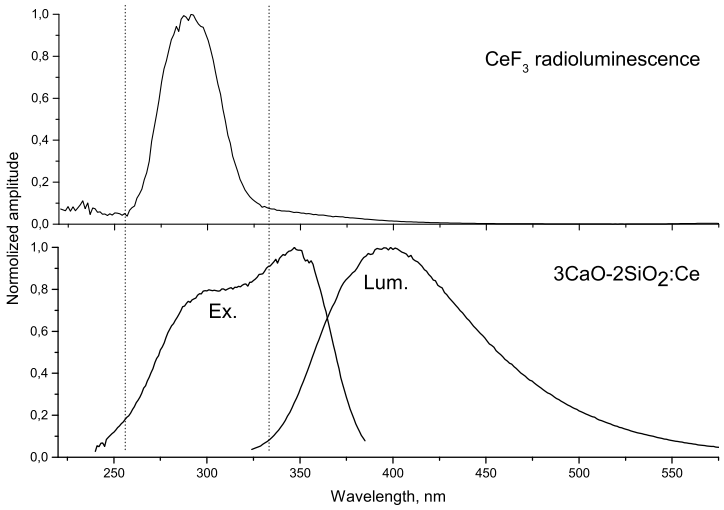

Figure 7: Upper panel, RL of CeF_3 crystal; lower panel, PLE (λem = 400 nm) and PL (λex = 300 nm) of CaO1 glass

prevent their final radiative recombination. Defects can also promote non radiative recombinations. Such processes are reasonably also related to the complex disordered glass structure, containing cations with different valence like Ca^{2+} and Si^{4+}. We do not exclude that high concentration of Ca^{2+} in the glass host also promotes fast non-radiative recombination of the free cariers created by ionizing radiation, as suggested by preliminary results obtained on other binary glasses with heavier alkaline earth ions like Ba^{2+} and Sr^{2+}. The involvement of defects is much less significant under intra-center excitation, resulting in bright photoluminescence emission in spite of a poor scintillation efficiency.

The favorable optical properties displayed by the considered glasses open the way for their future development in fiber form, to be employed in scintillation detectors as wavelength shifters.

Acknowledgements

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