

Luminescent properties of binary MO-2SiO₂ (M = Ca²⁺, Sr²⁺, Ba²⁺) glasses doped with Ce³⁺, Tb³⁺ and Dy³⁺

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Abstract

Binary alkali-earth silicate glasses doped with Ce³⁺, Tb³⁺, and Dy³⁺ were obtained by melt-quenching technique and their photo- and radio-luminescence properties were investigated. The disordered structure of the glass is responsible for an inhomogeneous broadening of the electronic radiative 5d¹ energy level of Ce³⁺ due to their localization in several positions with different surroundings, possessing a slightly different local ligand field. The influence of glass matrix composition on the Stokes shift as a function of ionic radius of the cation was shown. The radio-luminescence spectral shapes were related to the simultaneous occurrence of emissions from all Ce³⁺ configurations with relative weights proportional to their abundance in the glasses. The possibility of excitation of Ce³⁺ in different localizations was demonstrated and confirmed by the systematic shift of emission from excitation. On the contrary, no shift was observed in the Tb³⁺ and Dy³⁺ doped glasses, thanks to the lower effect of ligand field on their radiative electronic levels.

Introduction

Nowadays, single crystals are the most widely used materials in scintillation detectors [1,2]. However, active research is conducted also on other material forms like glasses, ceramics, or glass ceramics [3–5]. These allow realization of specific compositions and shapes that would be hardly reachable by single crystal growth. When doped with luminescent ions, glasses may display an effective luminescence signal and be promising candidates to substitute single crystals in different fields. In past years the possibility to obtain SiO₂-based fibers [6,7], BaO-2SiO₂:Ce (DSB:Ce) [8,9], Li₂O-2SiO₂:Ce (DSL:Ce) [10,11] and Li₂O-2SiO₂:Tb (DSL:Tb) [12] glasses with high scintillation efficiency was demonstrated. However, a number of problems are limiting the progress especially in the area of silicates [12].

Specific issues are the stabilization of rare-earth ions (REs) in the required valence state and their incorporation in high concentrations, in order to improve the transfer efficiency of excitations from the matrix. This problem may be solved by a few approaches during glasses production: i) to employ of special chemicals (for example SiC[13], (C₆H₁₀O₅)_n[14], that work as reducing agents); ii) to modify of the glass composition obtaining multicomponent glasses [15,16]; iii) to control the synthesis conditions (reducing or inert atmosphere)[17–19]. The above listed approaches allow to stabilize the RE predominantly in the required valence state and with

concentrations as high as 33 mol %. The second objective is related to the possible glass crystallization. The simultaneous occurrence of several types of RE-containing crystallites may take place during thermal treatments. In some cases their presence is detrimental because they lower glass transparency if their size exceeds few tens of nanometers [20]; moreover RE can be incorporated in a non-luminescent valence state (e.g. Ce^{4+} , Tb^{4+}). In other cases, the scintillation efficiency may be significantly increased by partial crystallization of glasses due to the formation of highly emitting crystallites. Such effect was previously demonstrated for DSL:Ce [21].

Ce^{3+} is widely used as a luminescent dopant in scintillators, mainly due to its short decay time and high scintillation efficiency [22]. In general, cerium ions may be incorporated in three different valence states (+2, +3 and +4) while they are contributing to the scintillation mainly in the +3 state. The preparation of silicate glasses containing only Ce^{3+} ions is a difficult task, because, especially for high contents, a part of them frequently tends to oxidize into the Ce^{4+} state leading also to a brownish coloration. The problem of stabilization of Ce^{3+} was also recognized in boron-silica and phosphate-silica glasses already for low activator contents [23,24].

Besides Ce^{3+} , other ions, like Tb^{3+} and Dy^{3+} can also be considered as luminescent dopants for applications in which a fast response is not required. Contrary to cerium, dysprosium and terbium can be easily stabilized in their trivalent state, independently on the atmosphere employed during thermal treatments in glass production. Both activators display sharp emission lines in the 350-650 nm spectral range, matching well the spectral sensitivity of silicon photo-multipliers (SiPM) [12,25,26].

We previously demonstrated that $3\text{CaO}-2\text{SiO}_2$ glasses, doped with Ce^{3+} ions, may be useful as wavelength shifters for UV emitting CeF_3 single crystalline scintillator [27]. Moreover, binary $\text{Li}_2\text{O}-2\text{SiO}_2:\text{Tb}$ glass was found to be a high light yield scintillator, promising for neutron detection [12], whereas $\text{BaO}-2\text{SiO}_2:\text{Ce}$ glass is considered as a prospective material to be applied in high energy physics detectors [9].

The aim of this work is the study of the photo- and radio-luminescence properties of disilicate $\text{MO}-2\text{SiO}_2$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) glasses, selectively doped with Ce^{3+} , Tb^{3+} or Dy^{3+} . $\text{MO}-2\text{SiO}_2$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) composition corresponds to the crystalline stoichiometric compound MSi_2O_5 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$); moreover, $\text{MO}-2\text{SiO}_2$ corresponds to the glass composition that is preferably formed at low temperatures in the $\text{MO}-\text{SiO}_2$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) systems. Doping with RE with d-f and f-f radiative transitions allows to evidence the influence of their nearest surroundings on the photo- and radio-luminescence properties.

Materials Preparation and Methods

CaCO_3 , SrCO_3 , BaCO_3 , CeO_2 , Dy_2O_3 , Tb_4O_7 and SiO_2 were used as starting materials. All reactants were analytical grade.

The glasses were synthesized by using melt-quenching technique. CaCO_3 , SrCO_3 , BaCO_3 (33.3 mol. %) and SiO_2 (66.7 mol. %) were mixed in required ratios and homogenized by milling in mortar. Glasses were melted in corundum crucibles of 50 ml volume for 2 h at 1450°C in FALORNI gas furnace (in CO-rich atmosphere). A RE oxide concentration corresponding to the substitution of 1 at. % of Ca^{2+} , Sr^{2+} or Ba^{2+} ions with a RE ion was adopted. The samples list is presented in Table I. The molten glass was casted on steel surface, and the obtained samples were annealed at 700 °C for 4 h in air for reducing the stresses before mechanical processing. Transparent and homogeneous glasses were cut and polished to obtain plates of 1 mm thickness.

Table 1. List of investigated samples. All samples were doped with 1 at% of the RE specified in the composition

Short name	Glass composition
CaCe	CaO-2SiO ₂ :Ce
CaTb	CaO-2SiO ₂ :Tb
CaDy	CaO-2SiO ₂ :Dy
SrCe	SrO-2SiO ₂ :Ce
SrTb	SrO-2SiO ₂ :Tb
SrDy	SrO-2SiO ₂ :Dy
BaCe	BaO-2SiO ₂ :Ce
BaTb	BaO-2SiO ₂ :Tb
BaDy	BaO-2SiO ₂ :Dy

X-ray excited radio-luminescence (RL) measurements were carried out with a custom made apparatus featuring a CCD detector (Jobin-Yvon Spectrum One 3000) coupled to a monochromator (Jobin-Yvon Triax 180) with 300 (spectral resolution 4 nm) or 600 (spectral resolution 2,5 nm) grooves/mm gratings. RL was excited by X-ray irradiation using a Philips 2274 tube operated 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.

Photo-luminescence emission (PL) and excitation (PLE) spectra were measured using a xenon lamp as excitation source, followed by a double monochromator (Jobin-Yvon Gemini 180 with 150 (spectral resolution 5 nm) or 600 (spectral resolution 2 nm) grooves/mm gratings), and recorded by a nitrogen-cooled CCD detector coupled to a monochromator (Jobin-Yvon Micro HR). For samples with Dy³⁺ and Tb³⁺ ions a KV418 filter was used for cutting the higher orders of the excitation bands.

All PL, PLE, and RL measurements were performed at room temperature (RT).

Results and Discussion

The RL and optical absorption spectra of all the studied samples are shown in Fig. 1.

RL spectra of CaCe, SrCe and BaCe glasses, presented in Fig. 1a, display the well known $5d_1 \rightarrow {}^2F_{5/2,7/2}$ transition of Ce³⁺ peaking at about 380 nm. Moreover, a shoulder at higher wavelengths (approximately at 420 nm), for which a defect origin can tentatively be suggested, is detected mostly in the spectra of SrCe and BaCe. SrCe and BaCe glasses are characterized by lower RL intensities with respect to the CaCe sample.

The differences of the alkali-earth metals ionic radii lead to the formation of polyhedrons with different sizes giving rise to different local fields experienced by the RE ions. Furthermore, the glass compositions can also affect the transfer process of the excitation from the matrix to the RE electronic levels, the RE luminescence efficiency, and even the valence state of the RE. These aspects will be the subject of future studies. The absorption spectra reveal only an absorption tail

increasing at low wavelengths. We also note slight red shift of the absorption tail in SrCe and BaCe samples with respect to CaCe.

In Tb^{3+} doped samples, a set of narrow lines is observed (Fig. 1b). Both ${}^5D_{3-7}F_j$ (in the blue region, $j=4, 5, 6$) and ${}^5D_{4-7}F_j$ emissions (in the green region, $j=3, 4, 5, 6$) are detected. The maximum RL intensity is observed for CaTb and SrTb glasses, whereas it was found 1.6 times weaker in the BaTb sample. In addition, a weak and composite RL emission with maximum at ~ 350 nm is detected. Its relative intensity increases by increasing the atomic number of the cation (Ca, Sr, Ba). It may be caused by intrinsic defects in the glass matrix, which are often also present in oxide crystals [22,28].

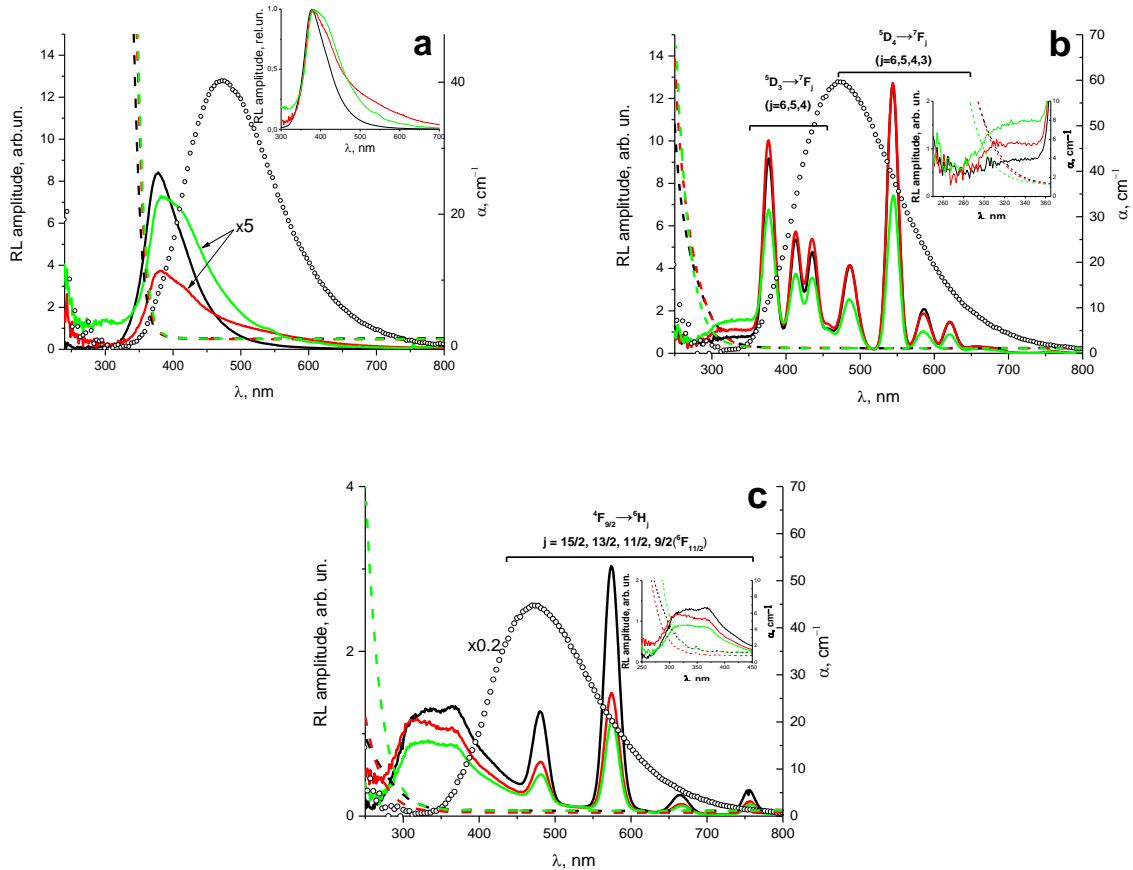


Figure 1. RL spectra for $CaO-2SiO_2$ (black line), $SrO-2SiO_2$ (red line), $BaO-2SiO_2$ (green line) glasses doped by Ce^{3+} (a), Tb^{3+} (b) and Dy^{3+} (c) ions. The dashed lines correspond to the absorption spectra. A RL spectrum of a BGO crystal is also shown for comparison (circles). Insets show details of the overlapping of absorption and RL spectra in UV range. The absolute intensities of all RL spectra can be mutually compared.

The optical absorption spectra are similar for both Tb and Dy doped samples. They display an increase below 300 nm, possibly caused by oxygen-vacancy defects [29]. Finally, four narrow lines are observed in the RL spectra for CaDy, SrDy and BaDy samples (Fig 1c). They correspond to the ${}^4F_{9/2} \rightarrow {}^6H_j$ radiative transitions of Dy^{3+} ions. Moreover, CaDy samples are characterized by an RL intensity twofold higher than that of SrDy or BaDy. A wide and composite emission with maximum at ~ 350 nm, similar to that detected for Tb doped glasses, is also observed. It has a small overlap with absorption bands of Tb and Dy ions, but seems to be completely quenched in Ce doped samples due to overlapping with Ce^{3+} absorption band. However, an opposite dependence of its intensity in Dy doped samples upon the atomic number of the cation, with respect

to Tb-doped samples, is noticed. Definitely, this band is not caused by optical transitions of the dopant ions while it has probably a defect origin. Thus, the observed differences in the behavior of its intensity in Tb and Dy doped samples are probably due to the presence of different defect concentrations.

PL and PLE spectra for CaCe, SrCe and BaCe glasses are presented in Fig. 2. All spectral features are related to electronic transitions between 4f and 5d levels of Ce^{3+} [27].

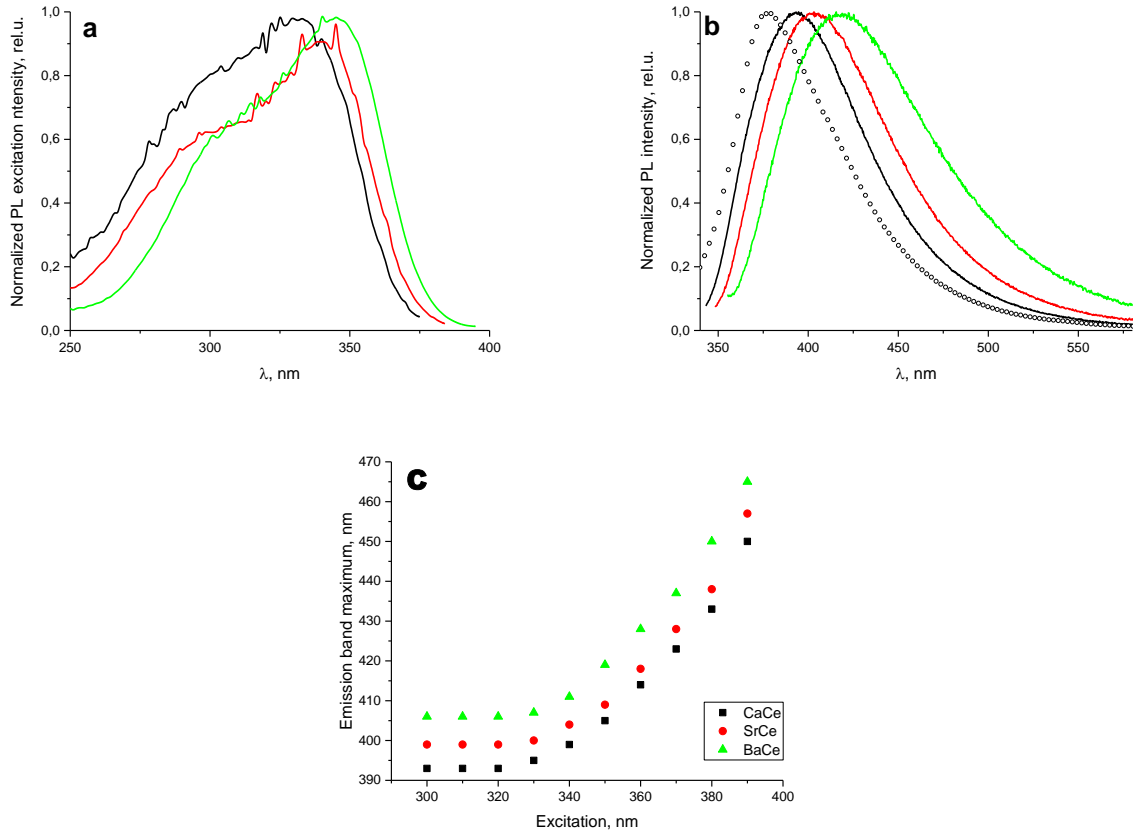


Figure 2. (a) Normalized PLE ($\lambda_{em} = 400, 408,$ and 420 nm for CaCe, SrCe and BaCe, respectively), (b) normalized PL ($\lambda_{ex} = 340, 345,$ and 350 nm for CaCe, SrCe and BaCe, respectively), and (c) dependence of the emission band maximum from excitation wavelength for CaCe (black), SrCe (red), BaCe (green) samples. In addition, the normalized RL spectrum for CaCe is shown in (b) (circles).

Alkali-earth ions, as well as Ce^{3+} , are incorporated in channel-like spaces within the glass network formed by connected $(SiO_4)^{4-}$ tetrahedra, which are orientated differently due to the specificity of the glass structure [31]. This kind of disorder is responsible for an inhomogeneous broadening of the electronic radiative $5d_1$ energy level of Ce^{3+} . Therefore, the broad excitations and emissions patterns observed in Fig. 2a) and 2b) are due to the presence of several slightly different contributions from Ce centers in different surroundings. This is also well depicted in Fig. 2c), where the modifications of emission bands position by changing excitation wavelength, are reported for each kind of glass.

Moreover, in Fig. 2c) an increase of the Stokes shift is observed by comparing CaCe, SrCe, and BaCe glasses. Such increase appears to be correlated with the increase of the ionic radii of the alkali-earth elements that, for a six coordination number, are $1.0, 1.18$ and 1.35 Å for Ca^{2+}, Sr^{2+}

and Ba^{2+} respectively [30]. The increase of ionic radius leads to the enlargement of the corresponding M-O (M = Ca, Sr, Ba) bond length so that, as a result, larger cations have a stronger influence on the glass network. The flat initial part of all the curves reported in Fig. 2c suggests the existence of a relatively dominant configuration of Ce centers displaying emission between 380 and 410 nm, according to the cation. On the other hand, the increasing part observed for higher excitation wavelengths is the fingerprint of the presence of several other configurations of Ce centers due to inhomogeneous broadening as above discussed.

Finally, a few comments are deserved to the shape of RL spectra. For all compositions, they appear peaked at around 380 nm, while a longer wavelength shoulder at about 420 nm is well evidenced especially for SrCe and BaCe glasses. It can be assumed that RL spectra are related to the simultaneous occurrence of emissions from all Ce^{3+} configurations with relative weights proportional to their abundance in the glasses; in this respect, they appear to be in a general agreement with the PL patterns, in which stronger low energy emissions are detected for SrCe and BaCe glasses.

At variance with the case of Cerium, we did not observe a significant difference of the peak positions in PL and RL spectra of Tb^{3+} and Dy^{3+} doped samples. Fig. 3 and Fig.4 show the comparison between PL and RL spectra of CaTb(a), SrTb(b), BaTb(c) and CaDy(a), SrDy(b), BaDy(c) samples, respectively. The origin of these bands is shown in Fig.1.

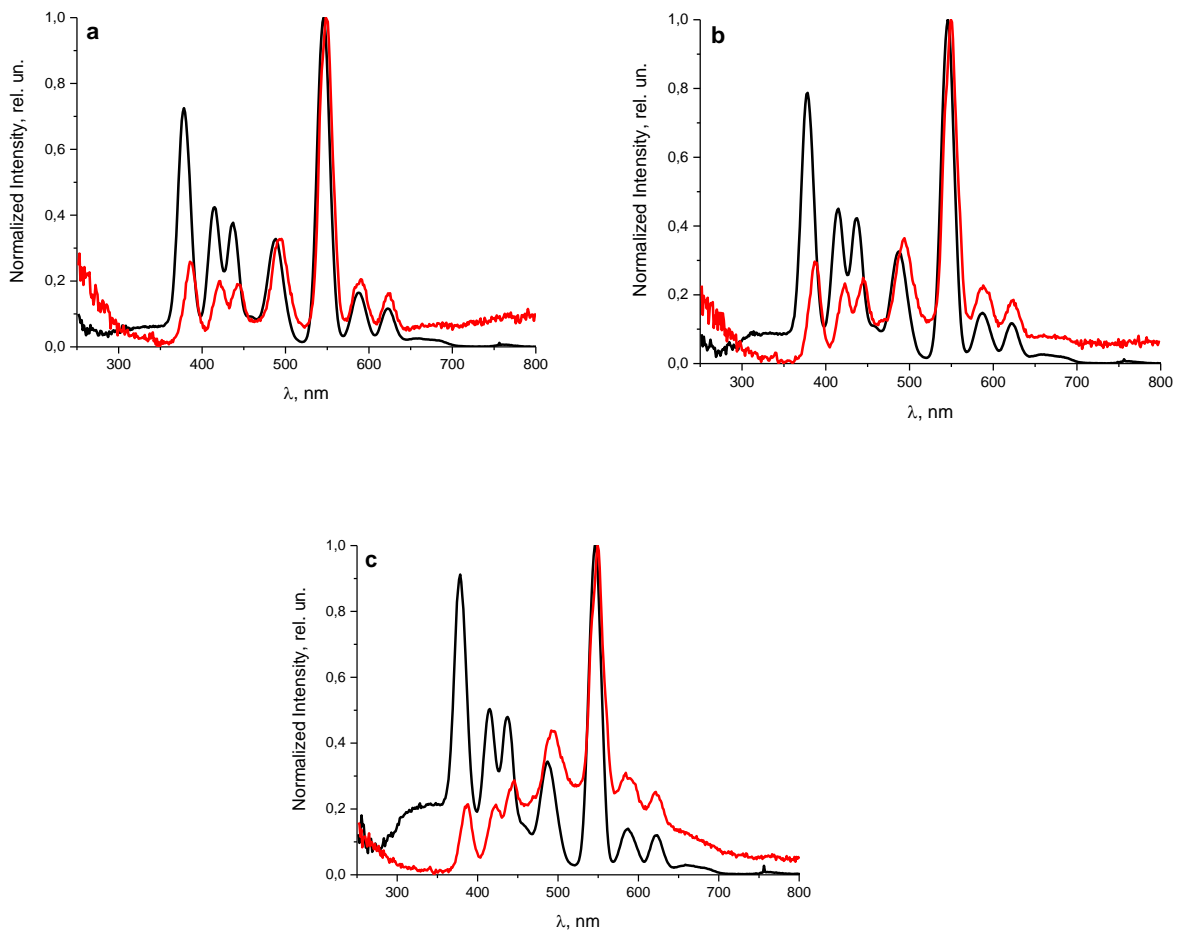


Fig.3 Comparison PL (excited at 277 nm, red line) and RL spectra (black line) for CaTb (a), SrTb (b), BaTb (c) is demonstrated.

The suppression of the blue Tb^{3+} emission on PL spectra versus the RL one is related to the presence of a KV418 filter in the PL measurement, to remove excitation light. Moreover, no shift of the lines was detected as a function of alkali earth ion, as expected due to the weak sensitivity of emission lines from the ligand field.

We did not find any dependence of the scintillation decay time kinetics on the kind of glass modifier MO ($M = Ca, Sr, Ba$). The decay constants were found to be close to measured values in [8,9]. The scintillation kinetics of Dy has a complex form, which is caused by the superposition of defect-centers and weak f-f luminescence of Dy^{3+} ions. On the contrary, scintillation kinetics of Tb^{3+} doped samples was found to be close to a single exponential curve with decay constant $\sim 2.5ms$ in all measured samples.

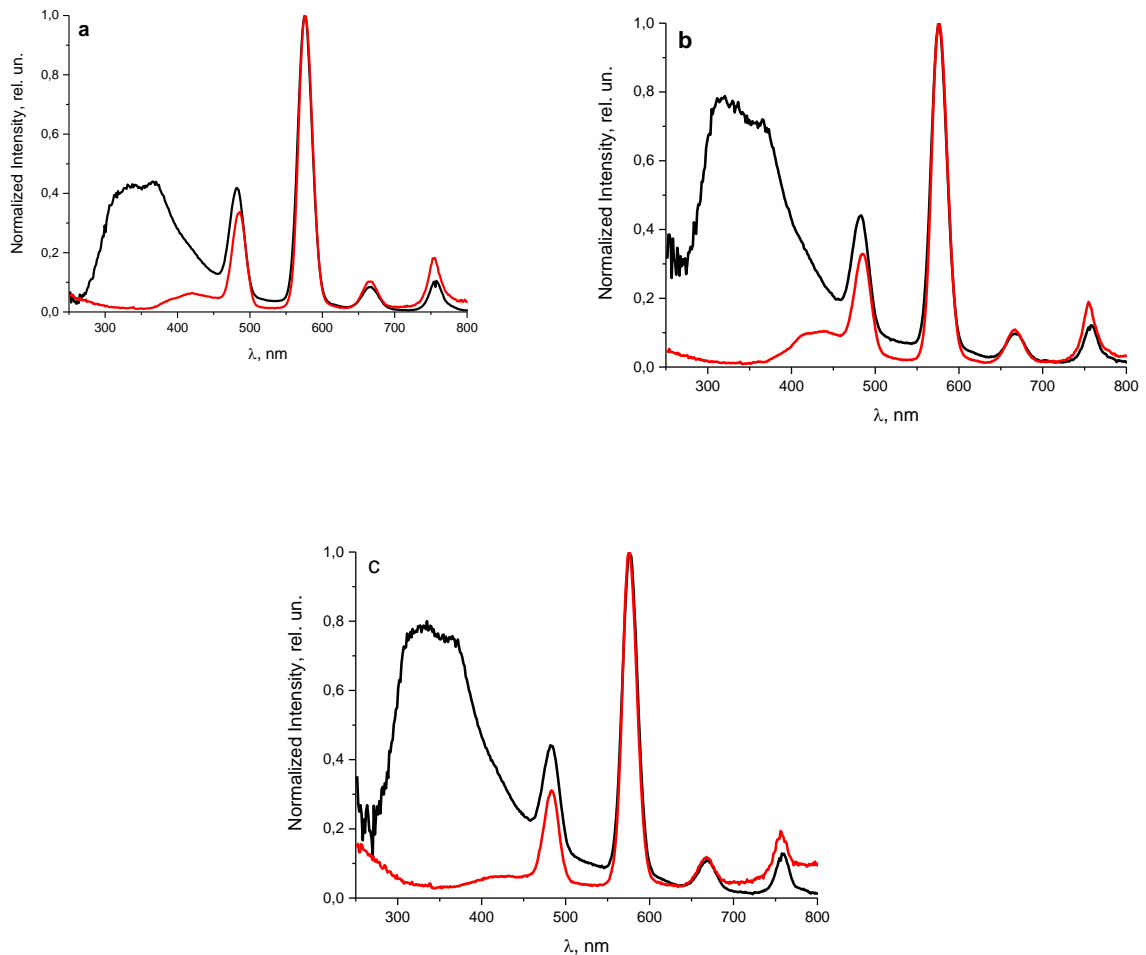


Fig.4 Comparison PL (excited at 350 nm, red line) and RL spectra (black line) for CaDy (a), SrDy (b), BaDy (c) is demonstrated.

Conclusions

We compared the radio- and photo-luminescence properties of binary $MO-2SiO_2$ ($M = Ca^{2+}, Sr^{2+}, Ba^{2+}$) glasses doped with Ce^{3+} , Tb^{3+} and Dy^{3+} , verifying the incorporation of these rare earth ions in the glass matrices in their optically active valence state. In the case of Ce^{3+} doping,

the spectral features turn out to be influenced by inhomogeneous broadening related to the amorphous structure of the hosts. In fact, a broad and composite emission was evidenced; moreover, the role of the ionic radius of the cation in perturbing the glass structure was evidenced by the increase of the Stokes' shift from CaCe, to SrCe, and BaCe.

The radio-luminescence spectral shapes can be tentatively related to the simultaneous occurrence of emissions from all Ce³⁺ configurations with relative weights proportional to their abundance in the glasses. Moreover, the emissions from the rare-earth ions are accompanied by a weak and composite emission with maximum at ~350 nm that may be caused by intrinsic defects in the glass matrix.

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