MO–SiO$_2$ and MO–SiO$_2$–Gd$_2$O$_3$ (M = Ca, Ba) Scintillation Glasses

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Abstract. Here we describe luminescent and scintillation properties of glasses of stoichiometric compositions: MO–SiO$_2$ and MO–SiO$_2$–Gd$_2$O$_3$ (M = Ca, Ba). It was shown that photo-excited luminescence spectra are systematically shifted to the long wavelength range in a comparison with radio-excited luminescence spectra. It shows that only a fraction of Ce ions took part in the creation of scintillation in the glass.

1 Introduction

There is a variety of inorganic scintillating materials which find applications as ionizing radiation detectors in medical imaging, security, geological exploration, high-energy physics, nuclear instrumentation etc. [1–3]. Most of these materials are used in single crystal or ceramic forms. Also glasses attracted the attention of researchers due to their combination of unique properties; they are in fact cheap to produce, environmentally friendly, transparent, and can be easily obtained in different forms: from bulks to fibers. With respect to crystalline compounds, glasses are also characterized by a lower concentration quenching [4] of the rare earth ions luminescence. However, the disordered structure of the atoms in glasses and the presence of the structural defects are the cause of low efficiency in the transfer of electronic excitation to emitting centers, thus preventing the achievement of high scintillation yields when the glasses are doped with suitable luminescence ions, like for instance Ce^{3+}. So far, encouraging results have been obtained with Ce-doped sol-gel SiO$_2$ [5, 6].

Among glasses, silicates look to be the most interesting in order to obtain new scintillation materials. Indeed, silica is a good glass forming compound, and crystalline silicates (notably oxyorthosilicates and pyrosilicates) already find numerous application as scintillating materials [7, 8].

It should be noted, however, that doping of pure silica glass with rare earth (RE) ions by using a standard melting method is a difficult task: the large difference in ionic radii, and the different coordination numbers of RE and Si ions result in difficult incorporation of RE ions in the silica matrix and a general tendency to RE segregation.

Moreover, RE doping can also result in the formation of defects acting as traps for free carriers in the silica matrix. These difficulties have been solved by using the sol-gel method to synthesize glasses with low RE contents, or by modifying the glass structure with the addition of other elements. Alkaline earth silicates are, in this respect, particularly attractive, since glasses with stoichiometric compositions can be obtained, leading to a lower probability of defect creation and higher radiation hardness. However, our studies shown that the scintillation properties of these binary glasses strongly depend on which alkali-earth cation is used.

In this paper we report comparisons among radio- and photo-luminescence spectra for a series of binary and ternary silicate glasses. We found that photo-excited luminescence spectra are systematically red-shifted with respect to the radioluminescence ones. This suggests that only a fraction of Ce ions takes part in the scintillation light emissions in these glasses.

2 Materials and Methods

2.1 Glasses Synthesis

MO–SiO$_2$ and CaO–SiO$_2$–Gd$_2$O$_3$ glasses doped with Ce^{3+} ions were obtained by heat treatment of a mixture of MCO$_3$ (M = Ba, Ca), SiO$_2$, Gd$_2$O$_3$, and CeO$_2$. CeO$_2$ was introduced by substitution of 1 at% of M^{2+} ions in glasses. The ratio MO:SiO$_2$ in glasses was 1:2, while for CaO–SiO$_2$–Gd$_2$O$_3$ glasses the components ratio was close to 1:2:0.34. The raw materials with 99.99% purity were weighed and homogenized in 20 cm^3 aluminum oxide ceramic crucible. The synthesis of the binary glasses was performed at 1450 °C in a gas furnace in a high concentration CO atmosphere for 2 h. The obtained bulk glasses were annealed at 500 °C for 4 h in a muffle furnace to reduce the stress. The ternary glasses have been obtained in a similar way but heating the raw materials at 1550 °C for 3 h and annealing at 600 °C for 4 h. The obtained glass blocks were colorless. Samples for the optical study were cut from the initial block in 1 mm thick plates and finished to an optical grade.

2.2 Samples Measurements

X-ray excited radio-luminescence (RL) measurements were carried out at room temperature with an apparatus featuring a CCD detector (Jobin-Yvon Spectrum One 3000) coupled to a monochromator (Jobin-Yvon Triax 180) with a 100 grooves/mm grating and covering the 200–1100 nm wavelength range. The excitation was performed with a Philips 2274 X-ray tube set at 20 kV and 20 mA. All X-ray irradiations were carried out in the same conditions with variable exposition time.

Steady state photoluminescence (PL) spectra were obtained at RT using a xenon lamp as excitation source coupled to a Jobin-Yvon Gemini 180 double monochromator, and recorded with a nitrogen-cooled CCD detector coupled to a monochromator Jobin-Yvon Micro HR.

3   Glass Forming in MO–SiO$_2$ (M = Ca, Ba) Systems

Among two-component systems, the MO–SiO$_2$ (where M = Ba, Ca) system has the most extensive glass forming region. This is seen from Fig. 1, which shows the diagram of states in the BaO–SiO$_2$ system.
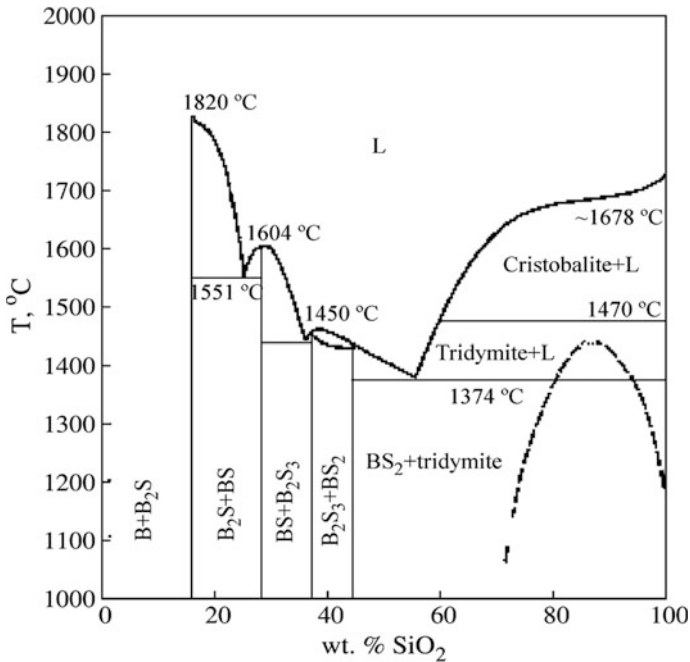

Fig. 1. Phase diagram of BaO–SiO$_2$ system [9]

A number of various compounds and eutectics forms exist in the system BaO–SiO$_2$ in a stable equilibrium [9]. It was found that stable stoichiometric compositions BaO–SiO$_2$ (BS); 2BaO–SiO$_2$ (B$_2$S), 2BaO–3SiO$_2$ (B$_2$S$_3$) and BaO–2SiO$_2$ (BS$_2$) with melting point 1604, 1700, 1450 and 1420 °C are formed. Even though the melting temperatures of these compounds are comparable to each other, the BaO–2SiO$_2$ composition is preferable because of its lowest temperature melting glass. In the case of CaO–SiO$_2$ system, there are also four stoichiometric compositions: CaO–SiO$_2$ (1544 °C); 2CaO–SiO$_2$ (2130 °C), 3CaO–2SiO$_2$ (1464 °C) and 3CaO–SiO$_2$ (2070 °C). Upper limit of vitrification is 50 mol% of CaO. The most interesting compositions are in the area of the eutectic with melting point of 1435 °C that is close to the composition CaO–2SiO$_2$.

4   Results and Discussion

BaO–2SiO$_2$ (DSB) glass and glass ceramics are well known scintillating materials [10]. It worth to note that the scintillation time decay of DSB:Ce glass is not particularly sensitive to the Ce^{3+} concentration until concentration quenching begins. The time decay can be well approximated using a sum of three exponential components. The decay is in fact composed by a fast 30 ns decay ($\sim$40% of total weight), an intermediate one ($\sim$50% of total weight) of about 180 ns, and 10%-component having decay constant in the range 250–350 ns. The presence of this slowest component in the scintillations depends both on Ce^{3+} concentration and on Ba/Si ratio in the matrix composition. The light yield of DSB:Ce sample with 662 keV ^{137}Cs gamma-source was found to be of the order of 100 photo-lectrons per MeV, in good agreement with previous results [10]. An increase of Ce content in the glass does not result in a proportional increase in the light yield of the material. One of the possible explanation is the Ce stabilization not only in a trivalent state, but also in tetravalent state in the glass, when the activator concentration reaches values of more than a few atom percents.

Contrary to BaO–2SiO$_2$, the calcium-silicate glass practically does not show any scintillation. However, the introduction of Gd$_2$O$_3$ in the glass composition dramatically increases radio-luminescence intensity, as clearly visible in Fig. 2. In pure binary system, the ratio between SiO$_2$ and CaO has been chosen from the point of view of the formation of stoichiometric compound with the lowest melting point in the glass-forming region. The composition of CaO–2SiO$_2$–0.34Gd$_2$O$_3$ glass was found experimentally. A further increase in the Gd$_2$O$_3$ quantity leads to a rapid increase of
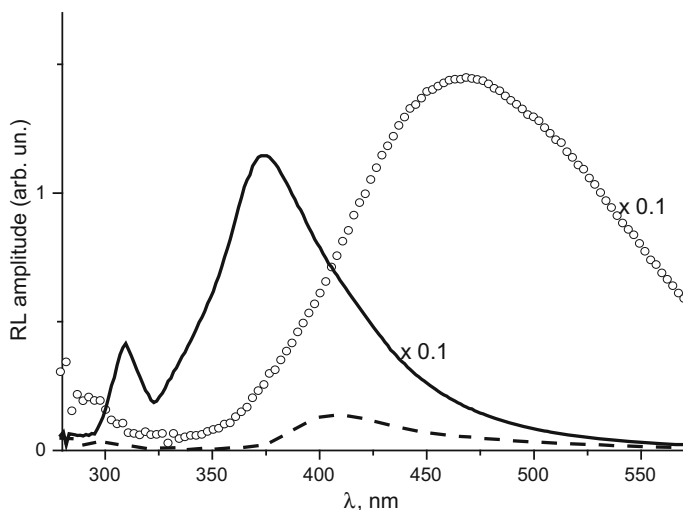

Fig. 2. Radio-luminescence spectra of glasses with composition 3CaO–2SiO$_2$:Ce (dashed line) and CaO–2SiO$_2$–0.34Gd$_2$O$_3$:Ce (solid line, spectrum is multiplied by 0.1) in comparison with BGO (marked as circles, spectrum is multiplied by 0.1)

glass melting temperature. As it can be seen from the spectra in Fig. 2, the Gd^{3+} luminescence is clearly visible at 313 nm, thus suggesting that Ce^{3+} luminescence sensitization through the Gd^{3+} subsystem is not completely effective.

Figures 3, 4 and 5 report comparisons between the normalized photoluminescence (excited in the first Ce^{3+} 4f-5d transition at 350 nm for all the studied samples) and radio-luminescence spectra of Ba–Si, Ca–Si and Ca–Si–Gd glasses, respectively.
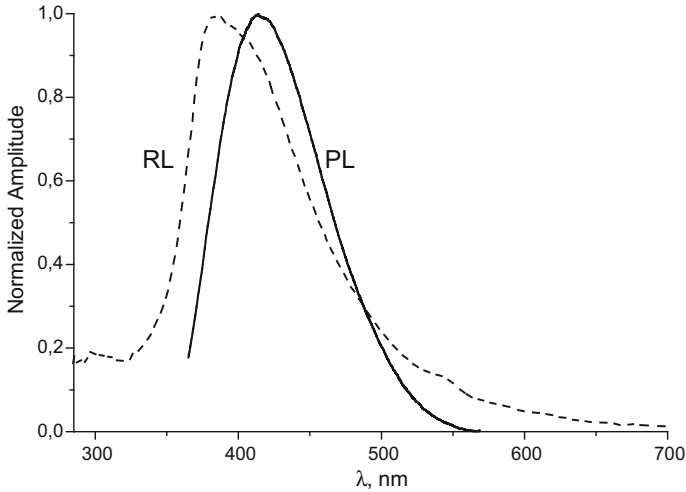
Fig. 3. Room temperature normalized radio-luminescence and photo-luminescence (excitation 350 nm) spectra of BaO-2SiO2 :Ce glass
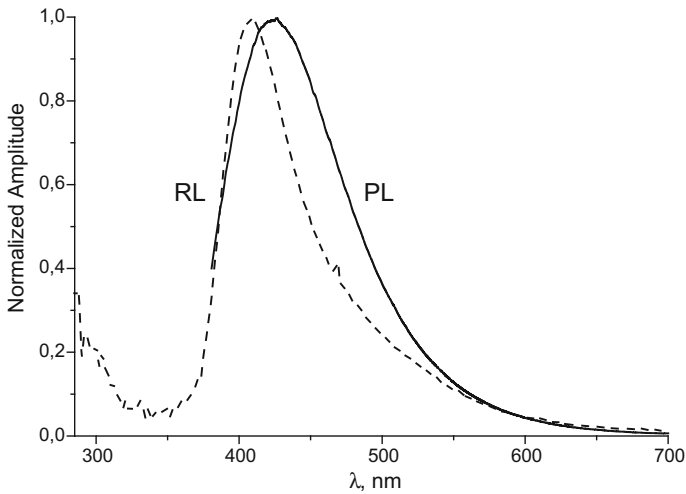
Fig. 4. Normalized radio-luminescence and photo-luminescence (excitation 350 nm) spectra of CaO–2SiO$_2$:Ce glass measured at room temperature
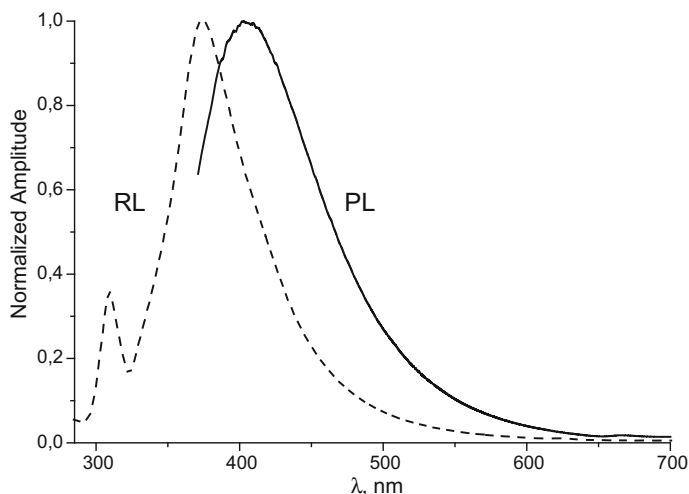
Fig. 5. Normalized radio-luminescence and photo-luminescence (excitation 350 nm) spectra of CaO–2SiO$_2$–0.34Gd$_2$O$_3$:Ce glass, measured at room temperature

A general difference has been observed between PL and RL spectra. The former are systematically shifted to longer wavelengths with respect to the RL ones. Since there is a series of different sites available for Ce^{3+} stabilization in the glass due to inhomogeneous broadening, one can rather safely suppose that also the Ce^{3+} luminescence properties are affected However, it seems that among all Ce^{3+} ions in the glass, only some fraction of ions, which has favorable conditions to capture free carriers, contribute to the scintillation. Thus, an increase of this fraction in Ce doped glass may be a prospective way for further increase of the glass scintillation yield.

5 Conclusions

Investigation of binary and heavy glasses doped with Gd showed that photo- luminescence spectra are systematically red-shifted with respect to those obtained in radio-luminescence. It seems that among all Ce^{3+} ions in the glass, only a fraction of ions, which has favorable conditions to capture free carriers, contribute to radio-luminescence. Thus, an increase of this fraction in Ce doped glass may be a interesting strategy to further increase the glass scintillation yield.

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