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High-efficiency SiO₂:Ce³⁺ glass scintillators

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We present the effect of a rapid thermal treatment (RTT) at high temperature (1800 °C) on the radio-luminescence properties of Ce-doped SiO₂ glasses prepared by the sol–gel method and previously densified at 1050 °C. Cerium concentrations ranging from 0.05 up to 1 mol% were considered. We found that, for all concentrations, the RTT induces a strong increase of the Ce³⁺ radio-luminescence efficiency; the x-ray-induced luminescence intensity of the SiO₂:0.1% Ce is about twice that of Bi₃Ge₄O₁₂. The decay time of the scintillation response, evaluated as ≈50 ns, is not affected by RTT. Infrared absorption measurements indicate that the luminescence increase cannot be related to significant release of OH groups during RTT. The conversion of Ce⁴⁺ ions into Ce³⁺ ions can also be ruled out since an increase of about 20% of the intensity of the 4.8 eV optical absorption band related to Ce⁴⁺ was observed after RTT. The occurrence of dissolution of rare-earth aggregates is suggested. © 2002 American Institute of Physics. [DOI: 10.1063/1.1524294]

In the lively field of scintillating materials research,¹ glass scintillators prepared by powder fusion and doped with rare-earth ions like Ce³⁺ or Tb³⁺ were studied for applications both in high-energy physics²⁻⁴ and in x-ray detection.^{5–7} In recent years, the sol-gel preparation method has also been considered, as a way by which it is possible to obtain glasses characterized by a high purity, at relatively low densification temperatures.⁸⁻¹³ The practical utilization of glasses seems to be limited by the presence of point defects acting as trap levels which limit the free carrier transfer from the matrix to the luminescent centers and also give rise to nonradiative recombination channels. In order to improve the scintillating performances of glasses, different routes can be followed: in analogy to what was observed in several crystalline systems,¹⁴ an increase of luminescence efficiency was successfully experienced in mixed Ce3+-doped GdPO₄-NaPO₃-based glasses where an energy transfer from Gd³⁺ to Ce³⁺ excited states was promoted.¹⁵ A complementary approach consists in the reduction of the point defect concentration: this result can be pursued by improving the starting materials purity and the stoichiometry conditions of the glasses. First results very recently obtained on sol-gel prepared Ce³⁺-doped SiO₂-based glasses densified at different temperatures up to 1050 °C¹⁶ accompanied by a strong reduction of the OH groups concentration¹⁷ revealed that densification up to 1050 °C leads to a much higher luminescence efficiency with respect to lower densification temperatures. Following this investigation line, in the present work, we show the effect of a postdensification rapid thermal treatment (RTT) at $T \cong 1800 \,^{\circ}\text{C}$ described next, by which it is possible to increase the Ce³⁺ luminescence intensity in a significant way. The x-ray induced radio luminescence (RL) and scintillation time decay characteristics of SiO_2 :Ce subjected to such a treatment are shown and compared to those of a glass subjected only to a densification process at T=1050 °C. Furthermore, due to the significant role played by OH groups in providing nonradiative recombination channels, the OH vibrational properties investigated by Fourier transform infrared spectroscopy are also presented.

Silicate glasses were prepared by the sol-gel method using tetraethoxysilane (TEOS) and Ce(III) nitrate as precursors. Ce concentrations from 0.05 up to 1 mol % were considered. An undoped sample was also prepared as a reference. The sol composition was obtained with a TEOS:H₂O:ETOH volume ratio of 1:0.6:3. The obtained sols, after gelation and subsequent drying in a thermostatic chamber at 35 °C, gave rise to xerogel monoliths. The xerogels were first densified up to 1050 °C. Two sets of samples were prepared. On one of them, a further RTT, was performed by using an oxidizing oxygen-hydrogen flame. Such a treatment typically features a very quick temperature increase (2-4 s) up to $1800\pm50 \text{ °C}$, where the sample is kept for approximately 10 s before a rapid cooling in air. The temperature was monitored by an optical pyrometer (Impac IE 120) working at 514 nm emission. The dimensions of the samples were approximately $5 \times 5 \times 1$ mm.

Moreover, for comparison a $7 \times 7 \times 1$ mm plate of $Bi_3Ge_4O_{12}$ (BGO) single crystal of high quality grown by Bridgman technique at the Shonan Institute of Technology, Fujisawa, Japan, was also measured.

X-ray excited radioluminescence (RL), ²²Na excited scintillation decays and IR optical absorption measurements were performed using apparatuses elsewhere described.^{16,17} RT optical absorption measurements in the 1100–185 nm

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FIG. 1. RT RL spectra under 20 kV x-ray excitation. Curve A, undoped SiO_2 ; curves B and C, 1050 °C densified SiO_2 :0.1% Ce before and after RTT treatment, respectively; curve D, BGO crystal. Inset 1 shows the dependence of RL intensity upon temperature for 1050 °C densified SiO_2 :0.1% Ce before and after RTT (full squares and full circles, respectively). Inset 2 displays RL intensity vs Ce concentration before RTT (filled squares) and after RTT (filled circles). The data are normalized to the intensity of SiO_2 :0.1% Ce after RTT. The error on the data does not exceed 20%.

wavelength interval were also performed, by a Varian Cary 50 spectrophotometer.

The effect of the RTT treatment on RT RL spectra is displayed in Fig. 1: curve A is relative to an undoped glass, which does not display any emission band under the present irradiation conditions; curve B refers to 1050 °C densified SiO₂:0.1% Ce and curve C to a similar glass after RTT treatment. For comparison, the RL spectrum of the BGO crystal is also reported [curve D]. The emission, centered at approximately 2.7 eV and related to $Ce^{3+} 5d-4f$ transition, is increased by a factor of 6 after the RTT treatment without significant spectral shape modifications. Thus, the RTTtreated glass displays a particularly strong luminescence, whose integral, in the present irradiation conditions, well exceeds that of a BGO crystal (by approximately a factor of 2). Moreover, the RTT treatment does not affect the temperature dependence of the RL as depicted in inset 1 of Fig. 1: one notes that only a slight luminescence quenching occurs at temperatures higher than 200 K in both cases (i.e., before and after RTT). Inset 2 shows the RL intensity versus Ce^{3+} concentration before (full squares) and after RTT (full circles). Before RTT, a marked decrease of the RL intensity is observed by increasing the Ce³⁺ concentration. Such a decrease might be explained either by a nonuniform incorporation of Ce³⁺ ions with the possible occurrence of aggregates, or by valence variations leading to the presence of Ce⁴⁺. These effects might become important already at relatively low concentrations well below 1%. After RTT, a strong RL increase is observed in all cases, with a less steep concentration dependence.

Moreover, scintillation decay measurements using a 22 Na source were performed at RT both before and after RTT. The results are shown in Fig. 2 for the 1050 °C densified glass [Fig. 2(a)] and for the RTT-treated one [Fig. 2(b)]. In both cases, the very fast component with time decay lower than 0.1 ns is caused by direct excitation of the photomultiplier cathode by gamma photons of the excitation source. The dominant decay component of about 50 ns is related to the allowed Ce³⁺ 5d-4f radiative transition, and its value is unaffected by the RTT treatment. The presence of decay



FIG. 2. RT scintillation time decays under excitation by 22 Na gamma source of SiO₂:0.1% Ce before (a), and after RTT (b). Thin continuous line, experimental data; thick continuous line, numerical fit.

components with a decay time comparable to or longer than the excitation gamma-photon frequency (20 KHz) is reflected in an increase of background level (before the rising edge of the decay curve) with respect to the true instrumental one measured after removing the sample. Slow decay processes, also named "afterglow processes," are due to delayed radiative recombination between electrons freed by defects acting as shallow traps and recombination centers (Ce⁴⁺ ions in this case).¹ The relevance of such decay components can be described by the use of the coefficient α reported in Fig. 2. It is defined as the ratio, multiplied by 100, of I_s (i.e., the difference between the signal level before the excitation pulse I_s and the true background, see Fig. 2) to the maximum intensity of the Ce³⁺ decay component I_{tot} . After RTT, α turns out to be around 2.5; this value, compared with $\alpha=3$ obtained prior to RTT, indicates that the RTT procedure slightly lowers the intensity of very slow decay components.

The enhancement of the emission intensity as a consequence of the RTT at a high temperature might be ascribed to several factors, like (i) a further decrease of the OH content in the glass, (ii) a conversion of Ce^{4+} ions into Ce^{3+} luminescent ions, or (iii) a dissolution of Ce-based aggregates. To monitor the possible role played by the residual OH, the infrared spectra of samples before and after the RTT were measured. Figure 3 shows the absorption spectra in the region of the OH combination (stretching and bending) modes for 0.05 and 0.5 mol % Ce3+-doped glasses. The peak at about 4521 cm⁻¹ is attributed to the silanol (Si-OH) combination mode: from the peak amplitude, the OH concentration was evaluated, following Ref. 18. For both Ce³⁺ concentrations, there are no meaningful changes both of the spectra (in Fig. 3, compare curve A with curve B, and curve C with curve D, respectively) and of the OH concentration, as a consequence of the RTT. In fact, the OH concentrations before and after RTT are 1.09 and 1.02 mol % for the sample with 0.5 mol % Ce, and 0.94 and 0.91 mol % for the sample



FIG. 3. Effect of the RTT on RT optical absorption spectra in the Si–OH combination mode region for samples with different Ce³⁺ concentrations. Samples doped with 0.5 mol %: Curve A before RTT, curve B after RTT. Samples doped with 0.05 mol %: Curve C before RTT, curve D after RTT. For clarity, curves A and B are shifted on the ordinate scale by 1.5 cm^{-1} . In the inset, the OH concentration (C^H_{OH}), as evaluated from the 4521 cm⁻¹ peak amplitude (according to Ref. 19), is plotted vs the thermal treatment temperature for samples doped with 0.5 mol % Ce³⁺ (stars) and with 0.05 mol % Ce³⁺ (open circles).

with 0.05 mol % Ce, respectively. It should be remarked that most of the Si-OH groups are already removed from the xerogel, as a consequence of the previous thermal treatments at temperatures below 1050 °C, as shown in the inset of Fig. 3, where the OH concentration is plotted as a function of the thermal treatment temperature. Therefore, the radiative emission enhancement induced by the RTT cannot be attributed to a further removal of OH. Alternatively, the possible conversion of Ce⁴⁺ ions into Ce³⁺ was also considered as a cause of the RL increase after RTT. The presence of Ce^{4+} was monitored by optical absorption measurements at RT. Preliminary results obtained on the sample doped with 0.05 mol % Ce showed that the intensity of the 4.8 eV band related to charge transfer transition of $Ce^{4+19-21}$ is slightly increased (\sim 20%) by RTT, indicating that this treatment gives rise to a small increase of Ce⁴⁺ ions in the glass. Thus, the observed phenomenology is more consistent with the occurrence, during RTT, of dissolution of Ce-based aggregates giving rise to a better dispersion of Ce ions, mainly in 3+ valence state (as evidenced by the strong RL increase) but also in the 4+ valence state (evidenced by the increase of the 4.8 eV band). It is worth noting that the tendency to the Ce aggregation is supported by the existence of regular Ce-Si–O structures as $Ce_2Si_2O_7$ (Ref. 22) or $Ce_{4.67}Si_3O_{13}$,²³ in which concentration quenching of Ce^{3+} emission is very likely. Moreover, trivalent rare-earth ion clustering was already observed in Eu³⁺-doped sol-gel silica glasses.²⁴ We remark that preliminary measurements performed on samples codoped with Gd³⁺ concentrations up to 8 mol%, showed the presence of an absorption peak at about 4250 cm⁻¹ which could be attributed to OH groups interacting with Gd clusters. Such a peak disappears if the sample is submitted to a RTT. Finally, the possible dissolution of Ce aggregates is supported by recently published data on diffusion of rare earths:²⁵ in the case of Yb³⁺, for example, the diffusion coefficient at 1800 °C is evaluated as 4.2 $\times 10^{-11}$ cm²/s which, in the RTT time interval, would allow for sufficiently large rare-earth movements of the order of 3000 Å.

In conclusion, the RTT performed on glasses already densified at 1050 °C appears to be a very significant tool in order to increase their luminescence performances. Further improvements of the emission intensity could be achieved if the residual OH amount (presently estimated as $\sim 1 \mod \%$) could be decreased by applying suitable chemical and physical treatments to the xerogels.

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