Radioluminescence and luminescence kinetics of fluoride glasses.

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Abstract: . Radioluminescince (RL) spectra of fluoride glasses (AFG, ZBLAN, HFG) have been measured under irradiation by 8 MeV . protons. Also luminescence time of fluoride glasses (HFG and HFG with Ce) have been measured. Luminescence have been excited by 180 keV electrons.

Introduction

A keen interest to the light emitting fluoride crystals and glasses primarily arises from their possible application as radiometric sensors. The principal advantage of the materials based on heavy metal fluorides with respect to the extensively used NaI crystals and organic scintillators is their fast response and radiation resistance [1-6]. The optical transparency of heavy metal fluorides in the infra-red range (up to 8 μm) is much higher than that of all other materials used. These glasses have relatively low vitrifying points (about 600 K). Their refractive index is close to the index of pure silica glass (1.5). Any chemical element can be used in the multi-component fluoride systems to produce glasses.

In the present study the radioluminescence (RL) spectra of fluoride glasses under high energy proton irradiation have been measured. Also luminescence kinetics has been measured

Results

The RL spectra of the following fluoride glasses have been measured during 8 MeV proton irradiation (flux $<2\cdot10^{12}$ p/cm^{2}s, dose rate $<5\cdot10^3$ Gy/s) at the EGP-10M proton accelerator (SSC RF –IPPE)
HFG- 54%$HfF_4$24%$BaF_2$3%$AlF_3$18%NaF1%InF_3,
ZBLAN-52%$ZrF_4$20%$BaF_2$4%$LaF_3$4%$AlF_3$20%NaF,
AFG-36%$AlF_3$12.3%$BaF_2$12.3%$SrF_2$12.3%$CaF_2$12.3%$MgF_2$12.3%$YF_3$2.5%LaF_3.

The spectra (see Figs. 1 and 2) consist of a broad band in the region of 250 to 550 nm with its maximum at 400 nm and series of sharp lines peaked at 318, 342, 363, 388, 400 nm for AFG glass, or 316, 337, 358, 381, 392nm for HFG glass, or 319, 342, 365, 388, 400 nm for ZBLAN glass. Doping with Ce eliminates the broad band, decreases the intensity of the sharp lines significantly and shifts the sharp lines. New bands at 310-320, 480-490, 520-530, 595-615 and 640-650 nm appear after doping with Ce, as is also a new series of sharp lines peaked at 425, 445 and 470 nm.

The intensity of RL does not depend on the dose up to 10^6 Gy. However, at the time of switching on the proton beam the intensity of RL 380 nm is about 30-50% higher than in the steady state. The characteristic decay time of RL varies from 30 s for ZBLAN glass to 200 s for AFG glass.

Luminescence kinetics of fluoride glasses HFG and HFG doped with CeF_3 5% was measured while being irradiated (using pulsed irradiation with pulse duration of 5 ns) by electrons with energy Ee=180 keV (installation "Radan"). Luminescence was fixed within the range of 250-700 nm, including an area of intensive luminescence, connected with Ce - 360-600 nm.. Quick and slow components of luminescence were revealed: $t_{q.}$= 25 ns., $t_{sl.}$= 600 ns.

Discussion

The broad band of RL originates from electron-hole recombination in shallow traps. The long-term evolution of this band after switching on the proton beam is connected with the warm-up heating on ~100 K. Temperature increase leads to nonradiative recombinations of charge carriers, resulting in partial extinguishing of luminescence The charge transfer to deeper centers prevents recombination in shallow traps. Therefore impurity of Ce also suppresses background luminescence.

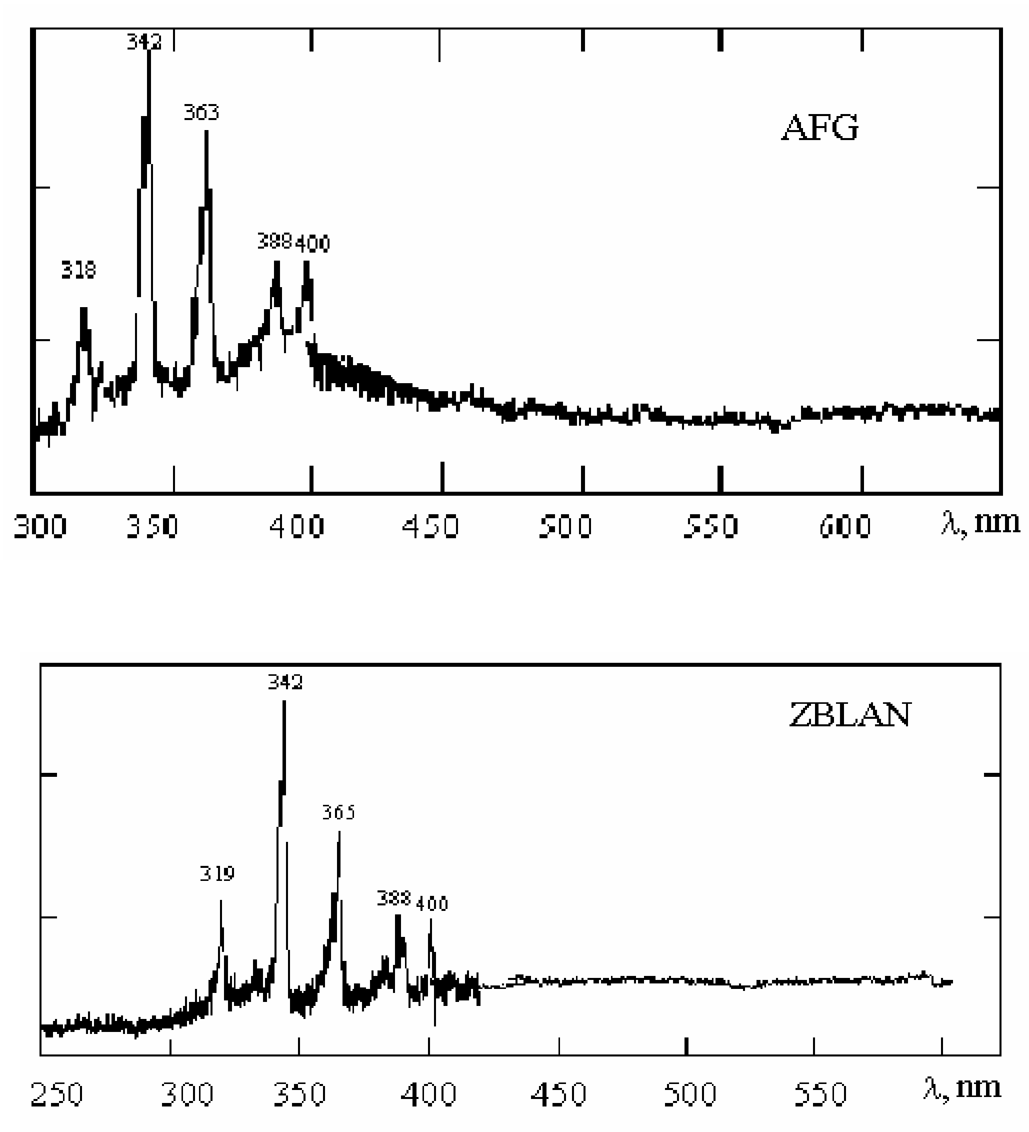

Fig.1. Spectra of RL of AFG and ZBLAN glasses under 8 MeV proton irradiation with the flux of $1.4{\cdot}10^{12}$ p/cm^{2}s.

It is conventional, that sharp lines observed in the UV region from 200 to 300 nm during irradiation of the glasses based on BaF_2 are due to crossluminescence. The light emission is excited due to core-valence transitions in Ba atoms [7-10]. The lines in the region of 320 to 360 nm are observed in the crystals and glasses based on BaF_2 and usually attributed to the decay of self-trapped excitons. However, the same position of the sharp lines in different glasses (310, 340, 360, 380, 390 nm) and no temperature effect evidence the light emission originating form core-valence transitions.

Effect of the doping with Ce on the sharp line positions is due to the change of the band gap. The light emission at the wavelengths of 310-320, 480-490, 520-530, 595-615 and 640-650 nm must be due to level-to-level transitions in Ce atoms. However, the mechanism has not understood yet. According to the papers [11-14], Ce-doped glasses emit light at other wavelengths, namely 290-310 nm, 340, 360 and 460 nm.

As shown in [15], increasing concentration Ce from 0.6 to 5 % decreases decay time of quick luminescence from 90 to 20 ns in BaF_2-CeF_3 crystals. This corresponds to the results of our experiments - decay time is 25 ns at contents Ce - 5%. On the other hand, slow component of luminescence t_{sl}.= 600 ns more corresponds to transitions, related to Ba, as, according to [16], there are two components of luminescence for BaF_2, decay time one is 0.6 ns, other - 600 ns.

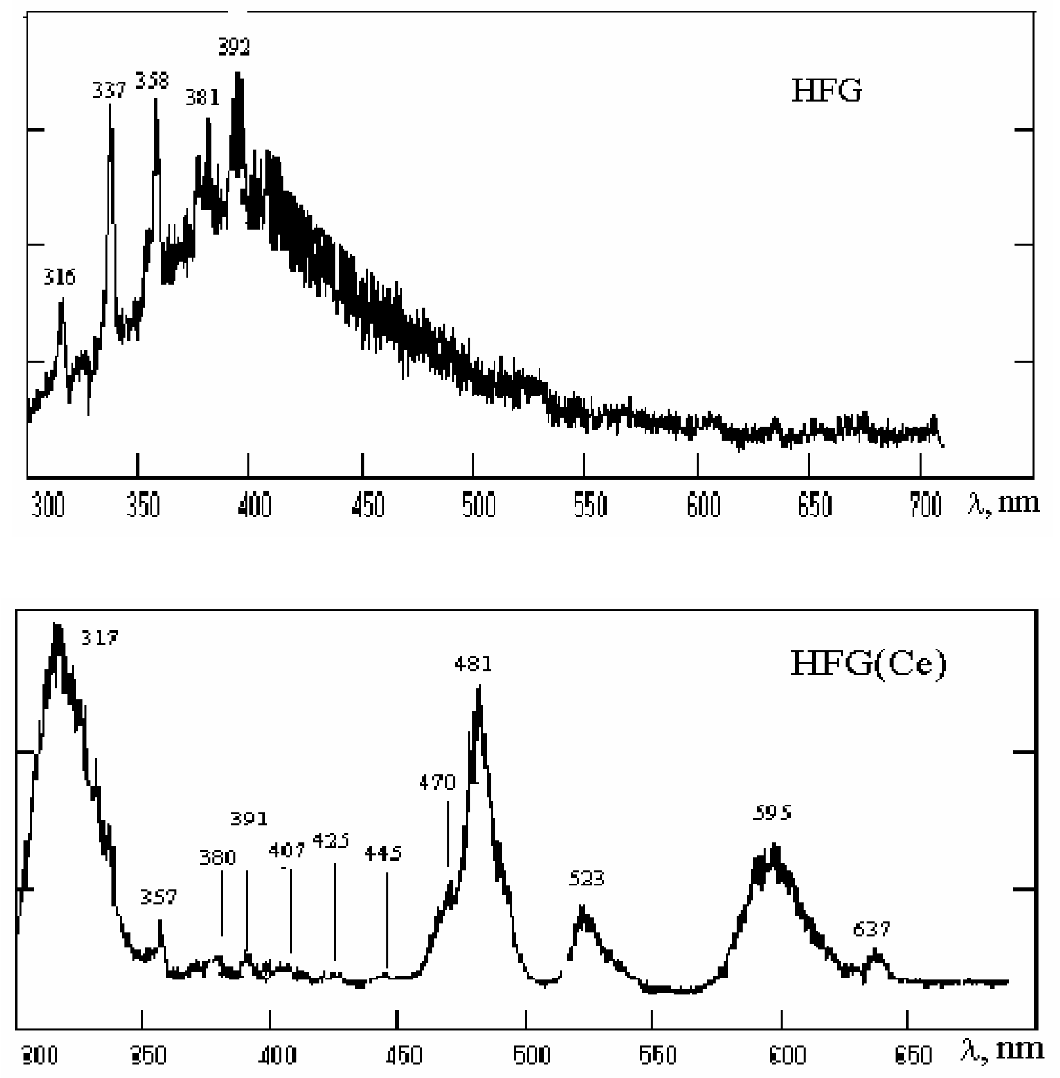

Fig.2. Spectra of RL of HFG and HFG (5%Ce) glasses under 8 MeV proton irradiation with the flux of $1.4{\cdot}10^{12}$ p/cm^{2}s.

Conclusion

The RL spectra of the glasses based on aluminum, zirconium and hafnium fluorides under 8 MeV proton irradiation (flux $<2{\cdot}10^{12}$ p/cm^{2}s) reveal the series of sharp lines (310, 340, 360, 380, 390 nm) attributed to core-valence transitions. Also, the RL spectra show the broad band (250-550 нм) caused by recombination of charge carriers in shallow traps. Doping with Ce results in, on the one hand, the suppression of the broad band of light emission and crossluminescence and, on the other hand, the appearance of the strong lines at 310-320, 480-490, 520-530, 595-615 and 640-650 nm , concerned with transitions on atoms Ce and Ba.

The sharp lines of UV and visible light emission are the promising features for application of the fluoride glasses as fast scitillators for radiometric.

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