

On the role of cerium in a chromium-ytterbium-erbium phosphate glass

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Abstract. The influence of cerium oxide on photo- and gamma-stability of chromium-ytterbium-erbium phosphate glasses is studied. It is found that UV irradiation does not cause any noticeable changes in the glass independently of the presence of cerium. Gamma rays produce colour centres in glasses without cerium and their lasing properties deteriorate. Doping glasses with an optimum amount of cerium oxide improves their radiation resistance with respect to gamma rays.

1. Introduction

It is known that to prevent the formation of colour centres in laser glasses irradiated by UV light or x-rays, these glasses are doped with elements of the variable valence such as titanium, antimony, etc. The most efficient dopant is cerium. Being in glasses simultaneously in two forms Ce^{3+} and Ce^{4+} and having absorption bands only in the UV region, cerium can be readily recharged upon irradiation by capturing charge carriers of one or other sign and thereby preventing the formation of colour centres in glass, which absorb light in the visible and IR spectral regions [1–3].

To our knowledge, the influence of cerium on the lasing and service properties of erbium glasses has not been studied so far. (True, some papers contain general statements that doping with cerium reduces solarisation or enhances the efficiency of flashlamp pumping [5]). The absence of such papers and also the assumption [6] about the possibility of using cerium as a stabiliser of the valence state of chromium ions stimulated this study. This study is urgent because at present erbium glasses are extensively used, and any opportunity to increase their efficiency and improve their operating parameters is of interest.

2. Influence of cerium oxide on spectral and luminescent characteristics

We studied three model compositions of phosphate glasses: Na – Al – La – P_2O_5 (composition I), Pb – La – P_2O_5 (com-

position II), and Ba – Al – La – P_2O_5 (composition III). The glasses were founded in quartz crucibles of volume 100 ml in a resistance heated furnace with a controllable atmosphere produced over the melt surface. The founding lasted for 6 h at the temperature from 1200 to 1350°C depending on the glass composition. The mixture was prepared from high purity reagents from the same batch.

To verify the influence of cerium on the spectral characteristics of chromium ions (its valence state), we prepared three variants of the mixture of composition I containing 0.2% Cr_2O_3 : without cerium, with 0.5% CeO_2 , and with 0.525% Ce_2O_3 . The latter mixture was prepared only to verify the results obtained in Ref. [6], where it was claimed that it is the addition of Ce_2O_3 rather than CeO_2 results in the stabilisation of chromium ions in the trivalent state.

We did not expect that the addition of cerium of other valence would affect the spectral characteristics of chromium because Ce_2O_3 is not a stable compound even at room temperature. Upon heating Ce_2O_3 is rapidly transformed to CeO_2 [7]. Therefore, before the mixture melting, i.e., before the moment when cerium can hypothetically affect the valence state of chromium, cerium will be in its stable form CeO_2 . Because the compound Ce_2O_3 is not commercially available, we synthesised it directly before the charge.

All the three glass compositions were founded simultaneously in an oxidising atmosphere. Fig. 1 shows the absorption spectra of glasses obtained. The spectrum of glass containing Ce_2O_3 completely coincides with that of glass containing CeO_2 . One can see that the absorption bands (except the cerium part of the spectrum) of glass without cerium (curve 1) and of glass containing cerium (curve 2) also coincide. These bands are identical to the absorption bands of Cr^{3+} , which means that cerium does not affect the absorption spectrum of chromium ions and, hence, its valence state. Note that despite strong oxidising conditions of the glass founding, no Cr^{6+} ions were observed. In this respect, our glasses differ from borate glasses, which exhibit, even having been founded under reducing conditions, an intense absorption band at 360 nm, which is typical for the $3d^0$ transition in Cr^{6+} .

The spectral properties of chromium ions strongly depend on the glass composition and conditions of its synthesis. As we reported earlier [8], in passing to the reducing atmosphere of founding, a part of chromium ions in a glass transfer to the state Cr^{2+} . This follows from Fig. 1, which shows the absorption spectrum of glass without cerium that was synthesised in the reducing atmosphere (curve 1'). One can see that the intensity of the absorption bands of Cr^{3+} decreased and a noticeable absorption appeared in the long-wavelength region.

Fig. 1 also shows the calculated absorption spectrum of Cr^{2+} (curve 3). Glasses of compositions II and III syntheses-

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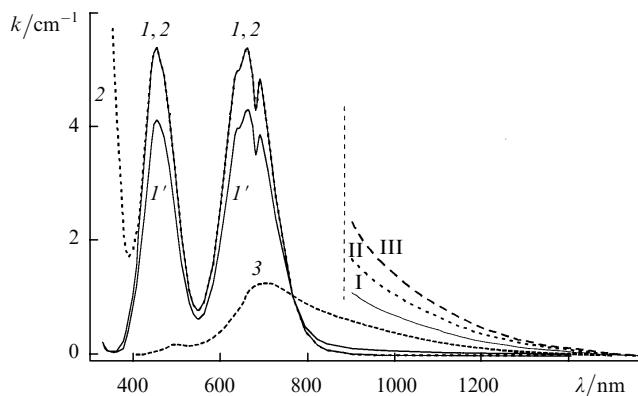


Figure 1. Absorption spectra of a glass without cerium oxide synthesised in the oxidising (*I*) and reducing (*I'*) atmosphere and a glass doped with cerium oxide synthesised in the oxidising atmosphere (*2*), and the calculated nonnormalised absorption spectrum of Cr^{2+} ions (*3*). Curves *I*, *II*, and *III* are the long-wavelength absorption wings of chromium ions for glasses of three compositions synthesised in the oxidising atmosphere (the ordinate axis scale is magnified by a factor of ten).

ised under similar conditions and at the same content of chromium oxide in a mixture exhibit a quite intense long-wavelength tail of the absorption band of chromium (curves *II* and *III* in Fig. 1). One can see that glasses of compositions *II* and *III* more strongly absorb in this spectral region than glass of composition *I*. This confirms the data [9] on the effect of the glass composition on spectral properties of chromium.

Because the long-wavelength wing of the absorption band of chromium ions overlaps with the luminescence band of ytterbium ions, it is obvious that energy transfer occurs from ytterbium ions to chromium ions [8, 10]. The rate of energy transfer should increase with increasing intensity of the long-wavelength absorption wing of chromium ions. This fact is confirmed by the measurements of the lifetime of luminescence of ytterbium ions (in the absence of erbium) for glasses of three compositions containing 20% Yb_2O_3 and 0.2% Cr_2O_3 synthesised in the oxidising and reducing atmosphere (Table 1).

One can see from the table that the lifetime of luminescence of ytterbium very strongly depends on the glass composition and the conditions of its synthesis, in complete agreement with the spectral properties of chromium ions considered above. The results of kinetic measurements presented in the Table 1 were obtained at 20 °C (it is known [10] that the rate of quenching of luminescence of ytterbium ions by chromium depends on the environment temperature). As for luminescence of chromium in phosphate glass, it is known that Cr^{3+} ions emit luminescence in the region from 750 to 1100 nm [5]. However, we have failed to detect luminescence of Cr^{2+} ions in the region from 1000 to 1600 nm [8], which suggests that the quantum yield of this luminescence is extremely low.

Table 1.

Glass composition	Lifetime of luminescence of ytterbium ions / μs	
	Oxidising conditions	Reducing conditions
I (without cerium)	1250	410
I (with cerium)	1200	400
II	700	200
III	500	100

Thus, the study of spectral and kinetic properties of chromium in a phosphate glass showed that these properties do not appreciable change upon addition cerium to the mixture both as CeO_2 or the unstable compound Ce_2O_3 .

3. Effect of UV radiation on lasing properties of an erbium laser

To establish the degree of influence of cerium on the output and operating parameters of an erbium laser, we compared active elements of size $\varnothing 2.5 \times 35$ mm made of an LGS-KhM glass developed in the Institute of Radio Engineering and Electronics, Russian Academy of Sciences (Moscow), and of two specially synthesised modifications of this glass. One of the modifications did not contain cerium, whereas the content of cerium in the second modification was three times greater than in a standard commercially available LGS-KhM glass. All the other parameters of the samples, such as the activator concentration, the degree of dehydration, and the reagent purity, were identical. All the glasses contained some antisolarisation additions.

Studies of the active elements showed that the presence or the absence of cerium in glasses does not affect the lasing threshold and efficiency. The threshold pump energy for all the active elements was 5 J and the differential efficiency in the free-running mode was 2%.

The UV irradiation was performed with an INP-3/45 flashlamp placed, together with an active element, inside a hollow silver-plated quartz reflector of diameter 12 mm. The external surface of the reflector was air-cooled. The repetition rate of 50-J flashlamp pulses was 0.25 Hz. To increase the fraction of UV radiation, the pulse duration was made $\sim 200 \mu\text{s}$. The active elements were taken periodically from the reflector and were tested for lasing in a quantron upon pumping by 6-J, 1-ms radiation pulses from an INP-2/35 flashlamp. Neither of the active elements showed the tendency of degrading energy parameters during the test time (10^5 pulses). Therefore, we can conclude that active elements made of a chromium-ytterbium-erbium phosphate glass do not degrade upon UV irradiation by flashlamps even in the absence of cerium ions in them, which is a specific feature of these glasses compared to neodymium glasses.

4. Influence of cerium oxide on the radiation resistance of glasses

To study the influence of cerium oxide on the radiation resistance of glasses, we synthesised glasses of compositions $\text{P}_2\text{O}_5 - \text{Na}_2\text{O} - \text{K}_2\text{O} - \text{Li}_2\text{O} - \text{Al}_2\text{O}_3 - \text{Yb}_2\text{O}_3$ with additions of erbium oxide (0.12%), chromium oxide (0; 0.04, and 0.08%), and cerium oxide (0–1%). The mixture was prepared from high purity reagents. The synthesis was performed in the dry oxygen atmosphere. The residual absorption of the OH groups did not exceed 1 cm^{-1} at the maximum of the 3000-cm^{-1} fundamental valence vibrational band.

To obtain integrated doses 10^5 and 10^6 rad, samples of thickness ~ 1 mm were irradiated by gamma rays from a ^{60}Co source with a dose power of 0.66 Mrad h^{-1} . The integrated dose of 10^4 rad was obtained from an x-ray source with a dose power of $0.036 \text{ Mrad h}^{-1}$. Spectral, kinetic, and lasing measurements were performed within two hours after removal of samples from the reactor.

Fig. 2 shows the absorption spectra of several samples recorded in the wavelength region from 350 to 700 nm before

and after irradiation by the integrated dose of 10^6 rad. One can see from the absorption spectra of a sample without chromium (curves 1 and 1') that losses in this spectral region increase due to a change in the glass matrix caused by irradiation. A similar effect is observed in the glass doped with chromium (curves 2 and 2'). A comparison of the absorption spectra of irradiated chromium-doped (curve 2') and undoped (curve 1') samples shows that the intensity of the absorption band of chromium decreases in the 400–550-nm region and increases in the 550–700-nm region after irradiation (cf. curve 2). This means that the valence state of chromium changes upon gamma irradiation: a fraction of Cr^{3+} ions transforms to Cr^{2+} ions whose absorption band has a maximum at 700 nm (see curve 3 in Fig. 1).

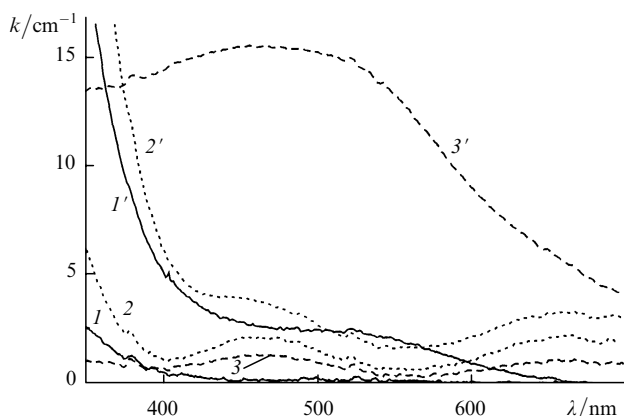


Figure 2. Absorption spectra of glasses before ($l-3$) and after ($l'-3'$) exposure to the gamma ray integrated dose of 10^6 rad. The content of chromium oxide in glasses was 0 ($l, 1'$), 0.08 ($2, 2'$), and 0.04% ($3, 3'$) and that of cerium oxide was 0.2 ($l, 1', 2, 2'$) and 0% ($3, 3'$).

Therefore, chromium ions, like cerium ions, are recharged under the action of ionising radiation, which is manifested in the change of their absorption spectrum. Like cerium, chromium prevents (however, far less efficiently) the formation of colour centres in a glass matrix. The protective function of chromium is demonstrated by comparison of the absorption spectra of irradiated chromium-doped and undoped glasses. One can see that the absorption coefficient of the undoped glass at 550 nm is higher than that of the glass doped with chromium, which should not be the case if the glasses had experienced the same changes.

A sample without cerium exhibits dramatic changes (Fig. 2, curves 3, 3'). For the integrated dose of 10^6 rad, losses at 500 nm increase to 16 cm^{-1} and their 'tail' is extended to 1000 nm, which should lead to a substantial shortening in the lifetime of luminescence of ytterbium ions, resulting in a decrease in the efficiency of sensitisation in the ytterbium-erbium pair.

Fig. 3 shows the dependences of the lifetime of luminescence of ytterbium and erbium ions in glasses on the integrated irradiation dose. The luminescence lifetime is normalised to its value for a given sample before irradiation. One can see that the lifetime of luminescence of ytterbium ions for samples containing cerium begins to decrease at the irradiation dose of 10^4 rad and for a sample without cerium, at 10^3 rad.

The influence of gamma rays on the lifetime of luminescence of erbium ions is far less pronounced. This is explained

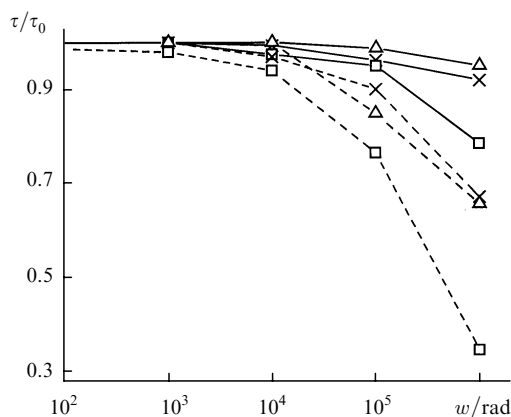


Figure 3. Dependences of the relative lifetime of luminescence of erbium (solid lines) and ytterbium (dashed lines) ions on the gamma ray dose for the CeO_2 content equal to 0 (\square), 0.2 (\triangle) and 0.8% (\times). The lifetime of luminescence is normalised to its value before irradiation.

by the fact that luminescence of ytterbium ions is mainly quenched by ions of divalent iron reduced by gamma rays [2] absorbing at 1100 nm and, as was established above, by ions of divalent chromium whose long-wavelength absorption wing overlaps with the luminescence band of ytterbium. Because the absorption of these quenchers at 1550 nm is substantially weaker, they affect the lifetime of luminescence of erbium ions in a lesser degree.

Thus, as in glasses doped with neodymium, doping chromium-ytterbium-erbium glasses with cerium enhances their radiation resistance. We also studied the dependence of the radiation resistance of glasses on the concentration of cerium ions and determined their optimal concentration.

We irradiated active elements of diameter 2.5 mm and length 35 mm made of an LGS-KhM glass and its modifications (without cerium) by integrated doses of 10^4 , 10^5 , and 10^6 rad. Studies of lasing showed that the parameters (the threshold pump energy and differential efficiency) of active elements made of an LGS-KhM glass did not change after irradiation by the integrated dose of 10^4 rad, whereas the efficiency of active elements made of the glass without cerium decreased by a factor of two and their threshold pump energy increased by 20%. Glasses without cerium exposed to the integrated dose of 10^5 rad completely lost their lasing ability, whereas the threshold pump energy of an LGS-KhM glass increased by 20–25%. After exposure to the integrated dose of 10^6 rad, active elements made of an LGS-KhM glass still retained their lasing ability.

5. Conclusions

We found that doping chromium-ytterbium-erbium glasses with a certain amount of cerium enhances their radiative resistance. The UV radiation of flashlamps does not affect noticeably the operating characteristics of active elements made of a chromium-ytterbium-erbium phosphate glass even in the absence of cerium ions in it.

The statement that cerium added to a mixture as Ce_2O_3 stabilises chromium ions in the trivalent state, thereby increasing the lasing efficiency of a chromium-ytterbium-erbium glass [6] has not been confirmed.

An LGS-KhM glass, which does not change its properties upon exposure to gamma rays, at least, up to the integrated

dose of 10^4 rad, can be used in various devices for special applications.

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