

Sensitization of the luminescence of rare-earth ions by trivalent iron in glasses

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A sensitization of the luminescence of several rare-earth activators through a charge-transfer state, $O^{2-} \rightarrow Fe^{3+}$, has been observed for the first time. The results show that the efficiency of this process can reach a value of unity in the Fe-Yb system.

The appearance of high-power optical pumping sources, which provide mainly ultraviolet light, has made it necessary to search for sensitizers capable of transferring the energy of this radiation to conventional activators. Of interest here is trivalent iron, which has an intense charge-transfer band corresponding to a transfer between oxygen and metal ions at $\lambda < 300$ nm and a metastable intraionic state at $\tilde{\nu} \sim 11\,000$ – $15\,000$ cm^{-1} (Ref. 1), above the initial "laser" levels of the basic rare-earth activators. However, the literature reveals no reports of such a use of this chemical element. We report here an attempt to bridge this gap.

Figure 1 shows the intrinsic absorption, luminescence, and luminescence excitation spectra of the gapless oxide glasses which we studied, activated with Fe^{3+} ions and coactivated with Nd^{3+} , Er^{3+} , and Yb^{3+} ions. Since the absorption in the visible part of the spectrum of the Fe^{3+} ions results from spin-forbidden intraconfigurational transitions, the absorption of the glasses with an iron impurity is due primarily to the charge-transfer band, whose long-wavelength edge is shown in Fig. 1a. In the luminescence of these glasses we observe two bands, with maxima at $\lambda \sim 490$ nm and 750 nm. The excitation spectra of these glasses in the ultraviolet region are essentially identical, while in the visible region for the long-wavelength band they are similar to the absorption spectrum of Fe^{3+} ions.¹ The latter fact and the presence of a remote exponential region on the luminescence curve at $\lambda \sim 750$ nm, with a constant lying in the range 1.2–3.5 ms, allow us to unambiguously link the long-wavelength luminescence with the decay of a metastable state of this activator. Further research will be required to determine the nature of the band at $\lambda \sim 490$ nm. All that can be asserted on the basis of the data available is that this band does not result from fluorescence from an excited charge-transfer state, since an estimate of its radiative duration on the basis of a calculation of the Kravets integral for the charge-transfer band yields a value at least two orders of magnitude smaller than the observed value. We see from parts b–d of Fig. 1, which refer to the glasses with identical mole concentrations of Ln_2O_3 which we studied, that the presence of iron gives rise to a luminescence excitation band of the rare-earth activators in a spectral region corresponding to the charge-transfer band. A calculation of the quantum yield of the transfer of excitations from the charge-transfer state to Ln^{3+} ions on the basis of the expression $\eta_c = I_{\lambda_{CTB}} \cdot k_{\lambda_{Ln}} / I_{\lambda_{Ln}} \cdot k_{\lambda_{CTB}}$, where I and k are the intensity and absorption index in the luminescence excitation and ab-

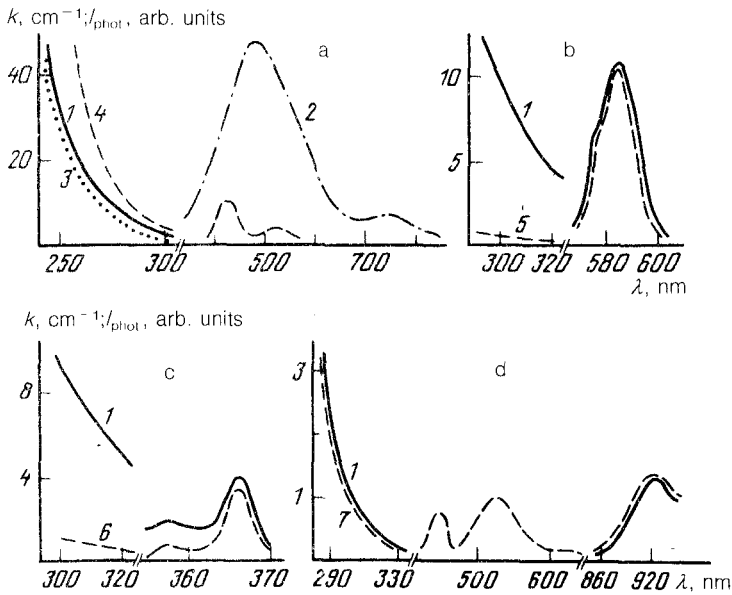


FIG. 1. Absorption spectra (1), luminescence spectra (2), and luminescence excitation spectra (3–7) of glasses activated with (a) Fe^{3+} ions and coactivated with (b) Nd^{3+} , (c) Er^{3+} , and (d) Yb^{3+} ions. 3–7— $\lambda_{\text{det}} = 490, 750, 890, 1500,$ and 978 nm, respectively. $T = 298$ K. The intensities of the spectral bands shown by curves 4 and 7 in the region 400–650 nm do not conform to the intensity scale in the ultraviolet region.

sorption spectra of the coactivators, shows that these quantum yields are about 5% and 10% in the neodymium and erbium glasses, respectively (parts b and c of Fig. 1). For Yb^{3+} ions under similar conditions, the yield is again close to 10%. As the concentration of trivalent iron is reduced an order of magnitude, η_c increases significantly, and in the ytterbium glasses it essentially reaches unity (part d of Fig. 1). The results would be difficult to explain without making some further assumptions, since the overlap integral of the absorption bands of these activators, with the luminescence spectrum of a glass containing iron, has the smallest value for the Fe-Yb system (Fig. 1, a and d). The luminescence band at $\lambda \sim 750$ nm shown in Fig. 1a apparently belongs to the transition ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ of quadruply coordinated Fe^{3+} ions, whose intensity is greater than that of the transition ${}^4T_{1g}({}^4G) \rightarrow {}^6A_{1g}({}^6S)$ of sextuply coordinated ions. At the same time, $[\text{FeO}_6]$ polyhedra should be predominant in the gapless glasses which were studied. The metastable state of the Fe^{3+} ions in these glasses is lower than that in $[\text{FeO}_4]$ polyhedra. The good resonance between the ${}^2F_{5/2}\text{Yb}^{3+}$ ions and the ${}^4T_{1g}({}^4G)$ states of sextuply coordinated Fe^{3+} ions and also the small minimum distance between these coactivators (according to a corollary of Pauling's electrostatic valence rule,³ they may be connected through oxygen bridge anions) are responsible for the effective sensitization in this system. Evidence in favor of this interpretation comes from the difference between the luminescence excitation spectra in the region corresponding to intraconfigurational transitions of trivalent iron (see curves 4 and 7 in Fig. 1, a and d) and the absence of any spectroscopic manifestations

of divalent ytterbium,⁴ capable of sensitizing the luminescence of trivalent ytterbium. If this is the actual situation, the lower value of η_c in the neodymium glasses would be explained on the basis that phonons must be absorbed during the transfer of excitations in order to compensate for the energy deficiency between the ${}^4T_{1g}$ (4G) state of the sextuply coordinated Fe^{3+} ions and the ${}^4F_{3/2}$ state of the Nd^{3+} ions. With regard to the sensitization of the luminescence of Nd^{3+} and Er^{3+} ions from quadruply coordinated Fe^{3+} ions, we note that it should not be effective since the latter cannot be part of the nearest cation shell of lanthanides, according to the corollary which we cited above.

We note in conclusion that, despite the photoreduction of trivalent iron by ultraviolet light⁵ and the accompanying increase in absorption in the near-IR part of the spectrum, an effective sensitization in the Fe-Yb system at exceedingly low ion concentrations may be of practical interest.

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