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Energy Transfer in Silicate Glass Coactivated
with Cerium and Ytterbium

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In a study of the optical properties of coactivated luminescent glasses, transfer of energy from UO_2^{2+} to $Nd^{3+(1)}$ and from Ce^{3+} to $Nd^{3+(2)}$ has been observed and it has been shown that for both of these ion pairs this energy interchange is partly achieved by radiationless transfer mechanisms. In this paper the transfer of energy from Ce^{3+} to Yb^{3+} in a lithium-magnesium-alumino silicate glass host matrix is reported and discussed.

Direct evidence for energy transfer from Ce^{3+} to Yb^{3+} is given by a comparison of the excitation spectra for 1.015 μ radiation in Figure 1. Inspection of these spectra clearly show the presence of a broad excitation band with a maximum around 0.3 μ in the coactivated glass (Figure 1B) which is not present in this glass singly activated with ytterbium (Figure 1A). It is also shown that this glass singly activated with cerium does not give rise to 1.015 μ radiation (Figure 1C). The 0.3 μ band is also an excitation band for the Ce^{3+} ultraviolet emission, which is strong in the singly-activated glass. Measurements of the excitation spectra for Ce^{3+} emission in these samples show that the reverse energy transfer, i. e., Yb^{3+} to Ce^{3+} does not occur. The magnitude of the Ce^{3+} to Yb^{3+} transfer is indicated by the observation that for the samples of the concentrations given in Figure 1, the Yb^{3+} emission spectrum excited by 0.313 μ radiation (Ce^{3+} absorption) is about twenty five times larger in the glass activated with Ce^{3+} and Yb^{3+} than in the glass activated with Yb^{3+} alone. Using samples with 0.01 cerium and 0.02 ytterbium, a corresponding increase considerably greater than one hundred is observed.

It is believed that the dominant mechanism of energy transfer is radiationless for two reasons: (1) a considerable shortening of the Ce^{3+} emission decay time is observed in the coactivated glass, and (2) a strong

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quenching of the Ce^{3+} emission is observed in the coactivated glass. For the concentrations of Ce and Yb shown in Figure (1), a decrease in the Ce^{3+} emission time from 70 to 50 ns is observed; however when the cerium concentration is increased to 0.01, a decrease from 70 to 15 ns is then noted. For the concentrations shown in Figure 1, the Ce^{3+} emission intensity is about seven times smaller in the coactivated glass than in the glass singly activated with cerium. The emission decay time of Yb^{3+} in this glass is about 900 μs , and does not seem to be strongly influenced by the presence of the cerium coactivator.

The energy level diagrams for these two ions in this glass matrix are shown in Figure 2. The Ce^{3+} absorption and emission spectra are shown as well as the background glass absorption; the side of the strong Yb^{3+} ultra-violet absorption band is also indicated. Possible Yb^{3+} luminescence between one of the 2D bands and the $^2F_{5/2}$ multiplet has been looked for in the spectral region from 0.25 to 0.5 μ but has not been observed.

The region of Ce^{3+} emission and Yb^{3+} absorption overlap appears centered about 29,000 cm^{-1} , but appreciable overlap exists from about 26,000 cm^{-1} to at least 35,000 cm^{-1} and it is possible that transfer may occur between even higher lying states. It seems clear that this is a case of radiationless transfer of energy between two rare earth ions which involve only states of the outer shell electronic configurations (probably 5d) followed by the inner shell emission of the Yb^{3+} ion ($^2F_{5/2}$ to $^2F_{7/2}$). The energy interchange takes place to the tail of a strong Yb^{3+} absorption band (4f to 5d) whose maximum occurs for wavenumbers greater than 50,000 cm^{-1} , and likely corresponds to the absorption in Ce^{3+} occurring around 33,000 cm^{-1} . Since the optical absorption coefficient for Yb^{3+} is 1 cm^{-1} or less in the region of Ce^{3+} emission, it would appear that radiative coupling between these ions plays a minor role in the energy transfer between these two ions in this host matrix. For the activator concentrations shown in Figure 1, a transfer time of about 170 ns is computed for these ions in this glass. This particular d band transfer should be of some theoretical interest in that it involves energy interchange from a one electron configuration (Ce^{3+} , $4f^1$) to a one hole configuration (Yb^{3+} , $4f^{13}$), a relatively simple situation.

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REFERENCES

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FIGURE CAPTIONS

- Figure 1 Room temperature excitation spectra for 1.015μ radiation from powdered lithium-magnesium-alumino silicate glass samples. Spectra uncorrected for incident intensity, but may be quantitatively compared.
(a) Activated with 0.02 cationic mole fraction ytterbium,
(b) coactivated, 0.0003 cerium and 0.02 ytterbium.
(c) Activated with 0.0003 cerium.
- Figure 2 Energy level diagrams for Ce^{3+} and Yb^{3+} in lithium-magnesium-alumino silicate glass. Wavy lines indicate radiationless transitions.

EXCITATION SPECTRA

Li Mg Al SiO₃ GLASS

1.015 μ Yb³⁺ EMISSION

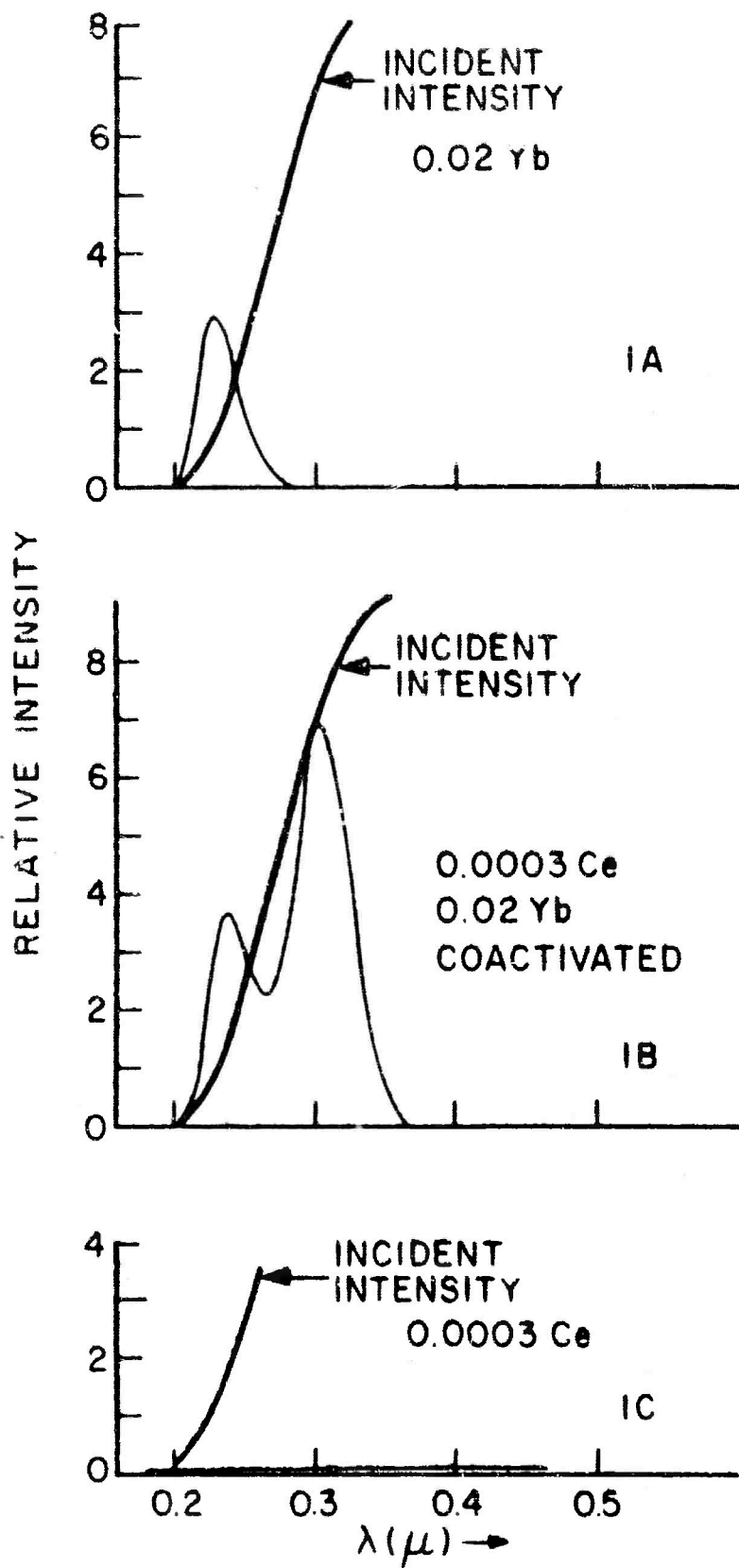


Figure 1

Li Mg Al SiO₃ GLASS

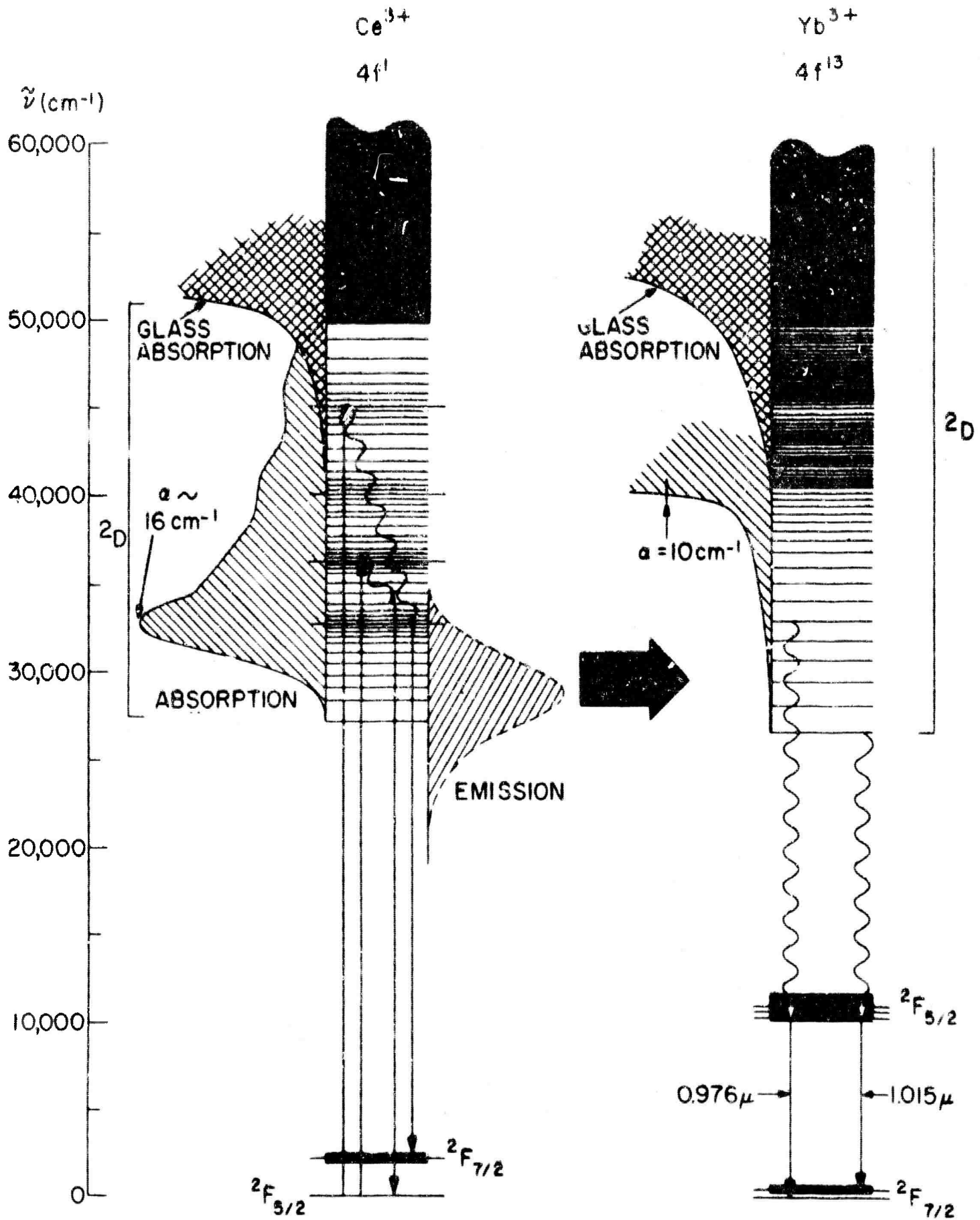


Figure 2