

Excited-State Absorption in Fluorescent Uranium, Erbium, and Copper-Tin Glasses*

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To observe the excited-state absorption in silicate glasses which contain UO_2^{2+} , Er^{3+} , or a copper-tin system, the glasses were excited to a long-lifetime state by pumping with a xenon flashtube. Absorptions from this excited state to higher states were monitored by a second flash. From these data, $\Delta\alpha$, the change of absorbance was calculated. Observations were made for wavelengths between 0.4μ and 1.1μ . Strong excited-state absorption bands appeared at 0.537μ in the UO_2^{2+} ion, and at 0.479μ in the Er^{3+} ion. In the copper-tin glasses, the effect decreased toward longer wavelengths.

INDEX HEADINGS: Glass; Fluorescence; Absorption; Uranium; Erbium; Copper; Tin.

THE excited-state absorption in silicate glasses of uranyl, trivalent erbium and what appears to be monovalent copper ion is discussed in this paper. Burke,¹ as early as 1898, observed the change of absorption in uranyl glass when its fluorescence was excited. Cross and Cross employed the saturation of the excited-state absorption in uranyl glass as a ruby laser Q -switch. Melamed *et al.*² similarly employed UO_2^{2+} doped into a Nd^{3+} laser glass to Q -switch the $1.06\text{-}\mu$ laser emission. Gires and Mayer,³ Aagard and Dufault,⁴ and Kiang *et al.*⁵ have examined the excited-state absorption and the ground-state deabsorption in ruby.

Excited-state absorption occurs when the active ions in the glass are excited into an upper metastable level from which further absorptive transitions to still higher levels are possible. In this paper we are primarily interested in the stronger transition from the metastable level that can be easily observed with the present equipment. In ions such as the rare earths, there are many possible excited-state absorption bands but most of these are not easily detected. If enough ions can be excited to the metastable state, then the number of ions remaining in the ground state is appreciably reduced, resulting in a decrease in the ground-state absorption. This effect is called ground-state deabsorption.

EXPERIMENTAL APPARATUS

Figure 1 shows the equipment that was employed to measure the change of absorption of glass rods. Typically, these rods were 6.35 mm in diameter and 76.2 mm long although shorter rods were employed, when the absorption was strong, to provide a maximum change of the transmittance. The rods were placed at the focus of a linear flashtamp in a cylindrical silvered cavity. Suitable inductors were employed to produce pump flashes with approximately half-sine-wave en-

velope. The light from the end portion of the U -shaped monitor flashtube was transmitted axially through the rod and was focused on the entrance slit of a Hilger-Watts constant-deviation monochromator. The monitor-flashtube intensity envelope was a fast-rise leading edge followed by an exponential decay. A photomultiplier was placed at the exit slit of the monochromator to determine the intensity of the transmitted light at a particular wavelength and its signal was displayed on one oscilloscope channel.

The revolving shutter opened immediately after the pump flash and permitted the monitor flash to pass through the monochromator. An adjustable electronic delay timed the monitor flash with respect to the pump flash.

Two phototubes (RCA 935) whose outputs were summed electrically measured the relative intensities from the two flashtubes and the sum was displayed on another channel of the oscilloscope.

EXPERIMENTAL PROCEDURE

To find the excited-state absorbance of a glass, the intensity of the monitor light transmitted through the monochromator was measured before and after the glass was pumped. Equation (1) was employed to compute $\Delta\alpha$, the change in absorbance after pumping, from the amplitudes measured from the oscilloscope traces.

$$\Delta\alpha = \frac{\ln[(T/T')(I'/I)]}{d} \times \frac{I_{p\text{ av}}}{I_p} \quad (1)$$

In this expression, T was the relative height of the monitor pulse at the exit slit and I was the relative height of this pulse from the phototube at the lamp. The primes indicate these same quantities when the rod was pumped. I_p was the relative height of the pump pulse and $I_{p\text{ av}}$ was the average of several measurements at the same pump energy. Equation (1) compensates for variations in the flashtube outputs.

THE URANYL GLASS

The Corning 2125 glass which contained about 0.5 wt% of UO_2^{2+} exhibited the excited-state absorption

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¹ J. B. Burke, Proc. Roy. Soc. (London) A76 (1905).

² N. T. Melamed and C. Hirayama, Appl. Phys. Letters 6, 43 (1965).

³ F. Gires and G. Mayer, Compt. Rend. 254, 659 (1962).

⁴ R. L. Aagard and R. A. Dufault, Appl. Phys. Letters 4, 102 (1964).

⁵ Y. C. Kiang, J. F. Stephany, and F. C. Unterleitner, IEEE J. Quantum Electron. 1, 295 (1965).

spectra shown in Fig. 2. From the emission and absorption spectra, the metastable level of the UO_2^{2+} ion in the 2125 glass was found to be in the vicinity of $20\,000\text{ cm}^{-1}$. The excitation or pump bands for the fluorescence in bulk pieces of the glass were centered around $21\,000$, $21\,700$, $24\,400$, and $30\,000\text{ cm}^{-1}$. The peaks in the excited-state absorbance occurred at $0.537\ \mu$ and corresponded to a level lying $38\,600\text{ cm}^{-1}$ above the ground state. A secondary maximum was present in the region of $0.750\ \mu$ which corresponded to a weaker excited-state absorption transition to a level $33\,300\text{ cm}^{-1}$ above the ground state. By shortening the monitor delay, it was possible to observe a large effect in the infrared.

The time-decay curves for the $0.550\text{-}\mu$ excited-state absorption and for the $0.523\text{-}\mu$ fluorescence were approximately exponential and closely coincided; both had lifetimes of about 0.5 msec . This showed that the fluorescence and the excited-state absorption originated from the same metastable level.

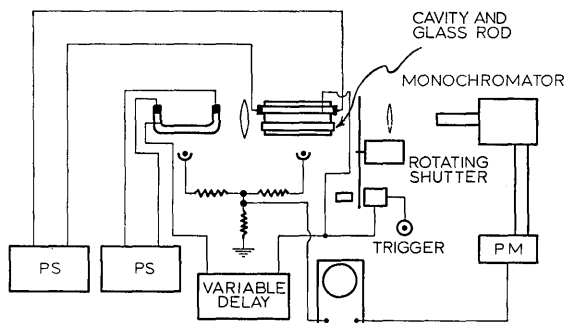


Fig. 1. Apparatus for measuring excited-state absorbance and ground-state deabsorbance.

McGlynn and Smith⁶ found absorption bands in uranyl nitrate hexahydrate in an aqueous solution in the vicinity of $34\,000\text{ cm}^{-1}$ and $>48\,000\text{ cm}^{-1}$ and tentatively assigned the designations ${}^1\Sigma_{0u}$ (or ${}^1\Delta_{2u}$) and ${}^1\Pi_{1u}$, respectively, to these levels. In the absence of ultraviolet absorption data for the glass, it was impossible to know if similar states were present. However, these states, shifted by the interaction with glass matrix, probably are the upper levels of the observed excited-state absorption bands.

THE TRIVALENT ERBIUM GLASS

The Er^{3+} ion in glass exhibits a relatively strong but narrow excited-state absorption around $0.479\ \mu$ which is many times larger than other possible excited-state absorption transitions in this ion for wavelengths between $0.4\ \mu$ and $1\ \mu$. Figure 3 shows the energy levels of the Er^{3+} given by Dieke⁷ for this ion in anhydrous

⁶ S. P. McGlynn and J. K. Smith, *J. Mol. Spectry.* **6**, 164 (1961).

⁷ G. H. Dieke, in *Advances in Quantum Electronics* (Columbia University Press, New York, 1961), p. 164.

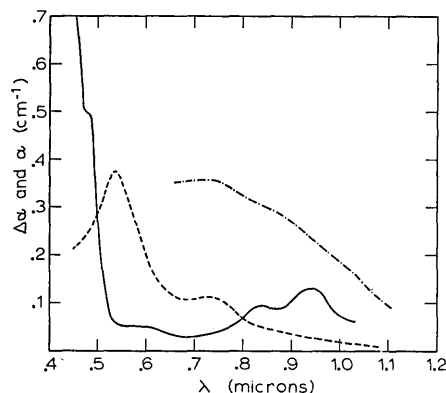


Fig. 2. Excited-state absorption of the Corning 2125 uranyl glass. — α ; ---- $\Delta\alpha$; pump: 270 J ; 1-msec pulse; delay: 1 msec ; - · - · $\Delta\alpha$; pump: 270 J ; 1-msec pulse; delay: 0.5 msec .

trichloride and closely approximates the levels in glass. It is useful to employ energy transfer between Nd^{3+} , Yb^{3+} , and Er^{3+} ions⁸ in glass as summarized in Fig. 3 to increase the pumping efficiency to the ${}^4I_{13/2}$ fluorescent state of Er^{3+} .

The $0.479\text{-}\mu$ excited-state absorption corresponds to a transition from the ${}^4I_{13/2}$ state to a region in the vicinity of the ${}^2K_{15/2}$ and ${}^2G_{7/2}$ of Er^{3+} . The ground-state absorption to these levels is of moderate strength and shows these levels smeared together by the ligand fields at room temperature.

This transition is both LaPorte and spin disallowed according to the quantum numbers assigned by Dieke; however, the transition is strikingly strong. It is apparent that an upper state of opposite parity, probably $5d$, is being mixed into the state through a static or a thermally induced odd potential term in the fields surrounding the ion thus making the transition forced electric dipole in nature. The strong spin-orbit interaction in rare earths breaks down the spin selection rule.

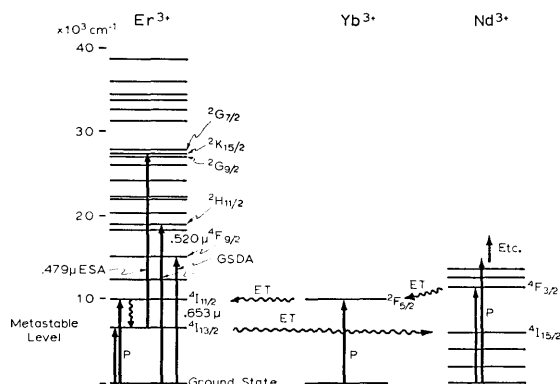


Fig. 3. Energy levels of the Er^{3+} - Yb^{3+} - Nd^{3+} system from data by Dieke.⁷ P, Pump transitions; ESA, excited-state absorption; GSDA, ground-state deabsorption; ET, energy transfer.

⁸ E. Snitzer and R. F. Woodcock, *Appl. Phys. Letters* **6**, 45 (1965). Er-Yb-Nd System; E. Snitzer (private communication).

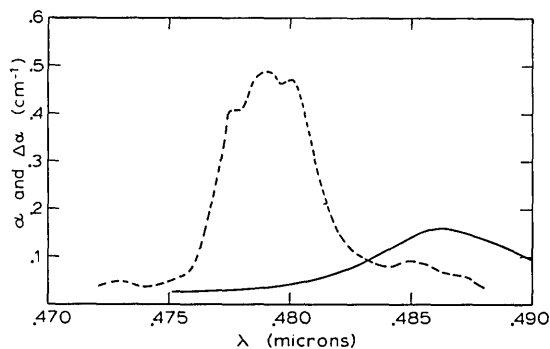


FIG. 4. 0.479- μ excited-state absorption band of MG 1515 Er-Yb-Nd glass. — α ; - - - $\Delta\alpha$; pump: 400 J; 1-msec pulse; delay: 1 msec.

The following experimental data were taken from MG 1515, a silicate glass which contained 1% by weight of Er_2O_3 , 10.5% Yb_2O_3 , and 0.25% Nd_2O_3 . The 0.479- μ excited-state absorption was also observed in silicate and in germinate glasses that contain only Er^{3+} . Figure 4 shows the excited-state absorption band at 0.479 μ . Resolution of the monochromator was about 5 Å and the precision of the measurements on the order of $\pm 2\%$. A lifetime of 13 msec was measured for the excited-state absorption, which corresponds quite well to the 14-msec lifetime for the 1.54- μ fluorescence from this glass.

Figure 5 shows the ground-state absorption and the ground-state deabsorption observed in the region of the 0.520- μ absorption band of Er^{3+} . The ground-state absorption is primarily produced by the Er^{3+} although about 1/40th is from the Nd^{3+} band present in this wavelength region.

From ground-state absorption data, we expect that an excited-state absorption between 0.514 and 0.520 μ should occur to one of the components of the ${}^4G_{11/2}$ state of Er^{3+} . The small positive $\Delta\alpha$ for wavelengths in the region of 0.515 μ is evidence that this excited-state absorption is present. The effect is weak and the negative $\Delta\alpha$ between 0.520 and 0.527 μ should be free of an opposing excited-state absorption.

Figure 6 shows the deabsorption effect observed in

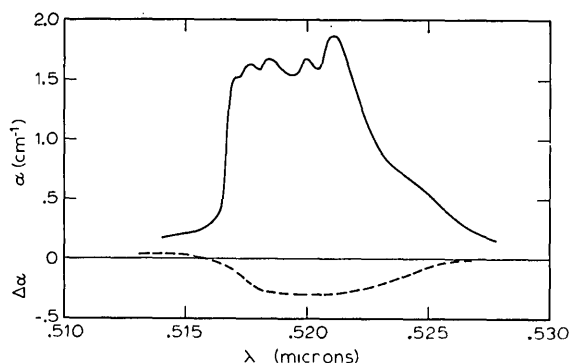


FIG. 5. 0.520- μ ground-state deabsorption band of MG 1515 Er-Yb-Nd glass. — α ; - - - $\Delta\alpha$; pump: 1000 J; 0.9-msec pulse; delay: 1 msec.

the 0.653 μ Er^{3+} band. Ground-state absorption spectra indicate that excited-state absorption bands should occur at 0.640 and 0.655 μ to the ligand-split levels of the ${}^4F_{5/2}$ Er^{3+} state. The positive $\Delta\alpha$'s around 0.640 μ correspond to the first of these bands while the positive $\Delta\alpha$'s at 0.670 μ are the tail of the excited-state absorption at 0.655 μ . This excited-state absorption is large, as shown by comparing the ratios of $\Delta\alpha/\alpha$ at .520 μ and at .651 μ under the same pump conditions of 1390 J. The deabsorption effect was found to be 40% less at 0.651 μ than at 0.520 μ .

The undoped base glass was checked for background excited-state absorption; it was found to be negligible at the wavelengths investigated. The cross section of the excited-state transition at 0.479 μ cannot be determined from these data because ground-state absorption spectra taken at 300° and 196°C to the ${}^4I_{13/2}$ level indicated that this state possessed several distinct levels of unknown degeneracy spread over 250 cm^{-1} . Furthermore, we do not know from which component the excited-state absorption is occurring.

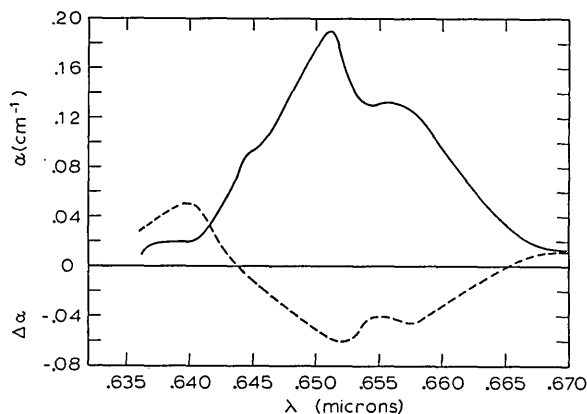


FIG. 6. 0.653- μ ground-state deabsorption band of MG 1515 Er-Yb-Nd glass. — α ; - - - $\Delta\alpha$; pump: 1390 J; 4-msec pulse; delay: 4 msec.

THE COPPER-TIN GLASS

Rodriguez *et al.*⁹ reported that this glass produced a phosphorescence with a lifetime on the order of a minute. Our glasses were made under reducing conditions and remained clear, indicating that the copper was primarily in the monovalent state, although there was evidence that some divalent copper was present. The glasses exhibited the long-term afterglow. These glasses solarize badly on exposure to ultraviolet; it was necessary to pump the rods with reduced energy. Both the excited-state absorbance and the transmittance decreased after each pump flash until an equilibrium was reached after 20 flashes. This indicated that the active ions were taking part in the solarization process.

The pump band was centered around 0.325 μ and

⁹ A. R. Rodriguez, C. W. Parmelee, and A. E. Badger, *J. Am. Ceram. Soc.* 26, 137 (1943).

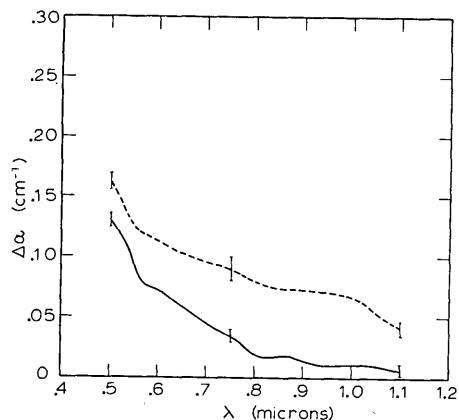


Fig. 7. Excited-state absorption of copper-tin glasses. --- SA-42; — SA-41; pump: 116 J; 0.3-msec pulse; delay: 0.5 msec.

the emission band at $.525 \mu$. The excited-state absorbance curves shown in Fig. 7 show results of averaging three measurements at $0.025\text{-}\mu$ intervals; the spread of points is shown at sample wavelengths. The excited-state absorbance of the SA-42 glass at 0.500μ was measured as a function of time. Initially the effect decayed to half its value with a time constant roughly equal to 10 msec and then remained constant to 1 sec. The lifetime is expected to be the same as that of the phosphorescence, or about a minute.

The copper-tin system in glass has not been extensively investigated and the nature of the phosphorescence and the excited-state absorbance is not understood. There are questions of which valency, either monovalent or divalent copper, produced the effects and what role the tin plays.

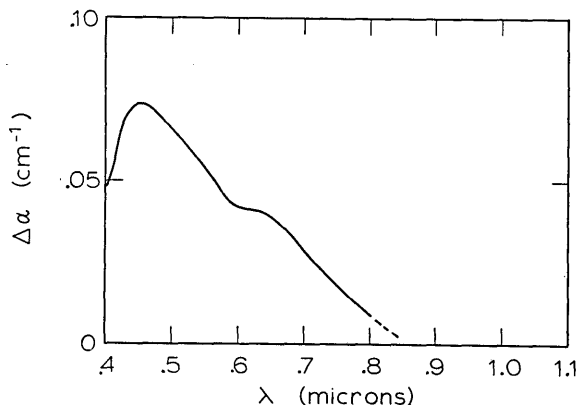


Fig. 8. Excited-state absorption of SA-26 silicate-glass. pump: 750 J; 0.4-msec pulse; delay: 0.2 msec.

SILICATE GLASS

During the course of these experiments it was discovered that a typical undoped silicate glass can exhibit an increase in absorption when flashed, as shown in Fig. 8. This effect had a short lifetime ($>0.1\text{-msec}$) and was proportional to the instantaneous pump intensity. The source of the excited-state absorption is unknown. The composition is given in the appendix.

ACKNOWLEDGMENTS

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APPENDIX

Glass Compositions

All compositions in relative weight percent (the totals may not be exactly 100%).

Uranium Glass

Corning 2125 Glass-Base glass is a soda lime silicate glass. From analysis: U = 0.46%; Si > 20%; Na > 15%; Ca > 10%; Al, Mg > 5% < 3%; B, Ba, Cu, Fe, Mn, Pb, Sr, Ti, Zr < 0.01%.

Erbium Glass

MG 1515: 1.0% Er_2O_3 ; 10.5% Yb_2O_3 ; 0.25% Nd_2O_3 ; 62.70% SiO_2 ; 0.93% Li_2O ; 6.73% NaO ; 10.18% K_2O ; 4.48% BaO ; 1.40% ZnO ; 1.40% Al_2O_3 ; 0.93% Sb_2O_3 .

Copper-Tin Glasses

	SA-41	SA-42
SiO_2	70.00	70.00
CaO	15.00	15.00
K_2O	11.80	8.60
Cu_2O	.80	1.60
SnO	2.40	4.80

Silicate Glass

SA-26: 65.58% SiO_2 ; 10.10% Na_2O ; 8.87% K_2O ; 9.58% CaO ; 1.98% Al_2O_3 ; 2.89% ZnO ; 1.00% Sb_2O_3 .