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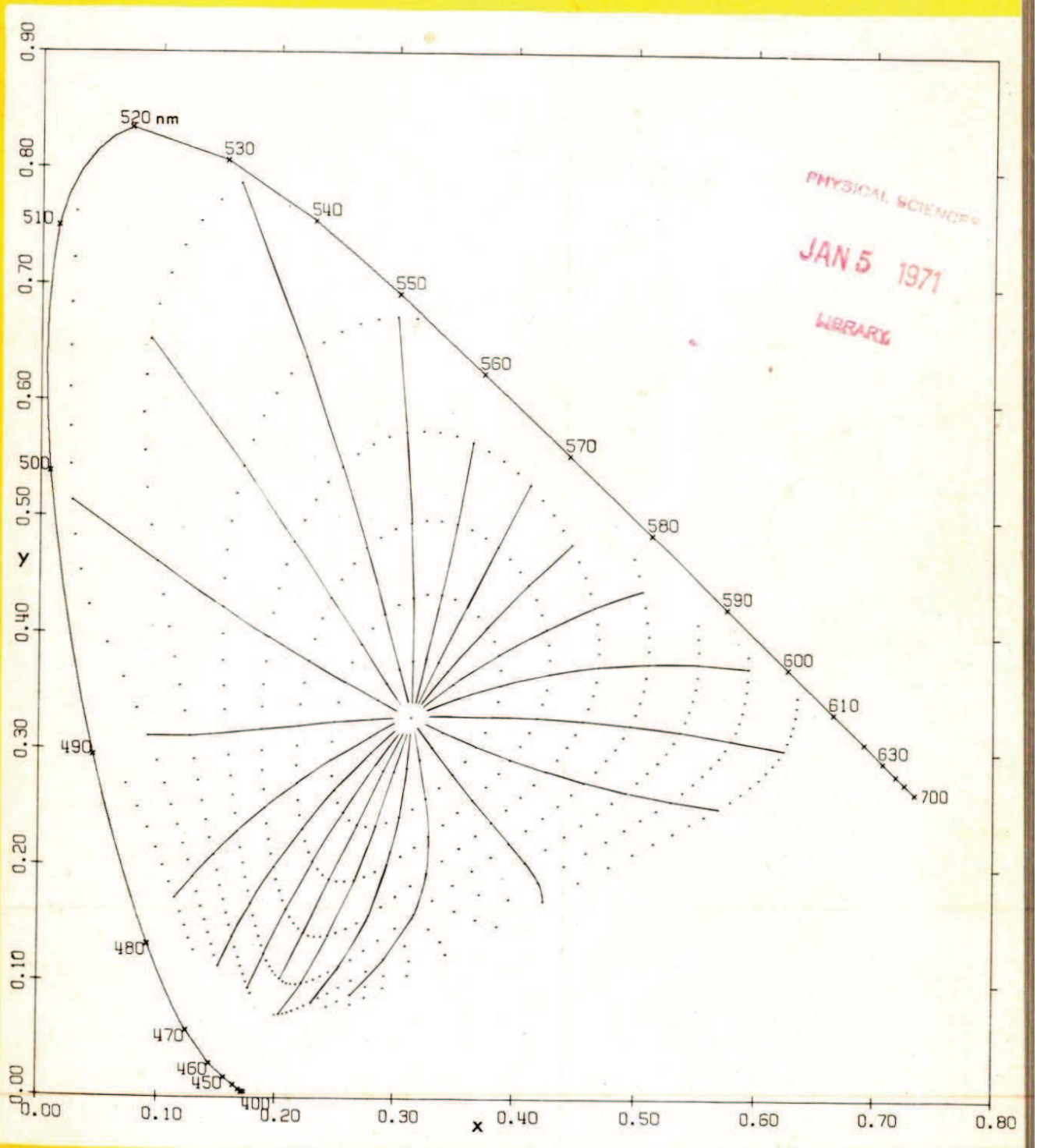

CHROMATICITY DIAGRAM

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Photoluminescent Conversion of Laser Light for Black and White and Multicolor Displays. 1: Materials

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A number of photoluminescent materials have been found to have properties that make them extremely useful for improving the quality of laser displays as well as offering simplifications for multicolor systems. The principal function of these materials is that of color conversion when coated onto a laser illuminated viewing screen. A secondary, yet significant, role is that of rendering the converted light incoherent. This eliminates the unpleasant granular or speckly texture associated with direct viewing of diffusely scattered coherent light. It is concluded that virtually any visible color may be achieved by photoluminescent conversion of a monochromatic blue or ultraviolet laser beam.

I. Introduction

In a recent review of laser display technology Baker[1] pointed out that considerable motivation in this field stems from the promise of producing a cathode ray tube type of display with essentially unlimited screen size. He concluded that although adequate light beam modulation and scanning techniques are presently available, broadly applicable equipment awaits the development of an efficient multicolor laser source.

Although such a multicolor source would indeed be desirable, the prospects for its realization, even in the distant future, are speculative. However, it is clear that efficient monochromatic or limited color range laser sources can and will be developed.[2] The purpose of the present work is to show that a monochromatic laser source is satisfactory for white light and multicolor displays when advantage is taken of photoluminescence, the absorption of light of one wavelength and the subsequent emissions at another wavelength. By properly coating a viewing screen with existing organic and inorganic phosphors it is possible to efficiently convert monochromatic blue or ultraviolet laser light into virtually any visible color including white. An additional benefit of this conversion is the elimination of the unpleasant granular texture generally associated with direct viewing of diffusely scattered coherent light,[3] because the converted light is incoherent.

The basic physics of photoluminescent conversion is quite simple. Photons from a light beam such as a laser beam are absorbed in a material which is thereby raised to an excited state. This excitation equilibrates in a brief interval, typically 10^{-3} sec to 10^{-8} sec. Equilibration can proceed both radiatively by the emission of a photon and nonradiatively by, for example, a series of phonon interactions. A material is considered to be a phosphor if radiative emission is observed. The relative strength of radiative transitions is specified in terms of the phosphor's quantum efficiency, defined as the ratio of emitted photons to absorbed photons. In general, the energy of the emitted photons is less than or equal to the energy of the absorbed photon (Stokes's law). That is, the color of the emitted light is either unchanged or shifted in the direction of longer wavelengths. In certain limited cases anti-Stokes (shorter wavelength) emission is also possible when additional energy is supplied to the single photon excited state by other means such as thermal excitation or multiple photon absorption.[4] In the present work we will consider only Stokes emitting phosphors which have sufficiently high quantum efficiencies to be of interest for laser display applications. Some emphasis will be placed on those materials that can be excited by the argon ion laser which is presently the most suitable source for a laser display system.

II. Characterization

There are four basic properties that characterize photoluminescent materials. They are (1) absorption and emission spectra, (2) conversion lifetime, (3) quantum efficiency, and (4) absorption cross section. It should be noted that the last three properties can be functions of the exciting wavelength. The features that make a phosphor desirable for application in laser display systems can be related to these properties. First, the phosphor must have a high absorption cross section for the exciting laser wavelength so that nearly total absorption can take place in a thin layer of material that is coated onto a screen. The phosphor should have an emission spectrum in a desired wavelength

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range with a high quantum efficiency, say, 50% or greater, since the display screen size is limited by available light intensity. In addition, the conversion lifetime should be sufficiently short so that the screen will not be overly persistent; there is no perceptible consequence if the lifetime is exceptionally short.[5] Finally, the phosphor should be inexpensive, stable, and preferably nontoxic.

III. Materials

Rather than attempting to cover the broad field of phosphors, we will discuss, by way of particular examples, those materials that we consider to be particularly suitable for laser display systems. They generally fall into two categories, inorganic rare-earth phosphors and organic dye phosphors. To a lesser extent we will also consider inorganic compounds that are activated by transition metals and other organic materials such as the aromatic hydrocarbons.

A. Inorganic Phosphors

According to Pringsheim,[6] practically all molecules that are photoluminescent in condensed states are rather complex. The only exceptions are the positive ions of some rare-earth metals. The optical properties of these ions are so little perturbed by the surrounding medium that, even in crystals, they behave almost like isolated atoms, and their energy levels are well known.[7] The rare-earth Tb^{3+} is a particularly useful ion since the wavelength for maximum absorption of its $^5D_4$ manifold corresponds quite closely to the blue (4880 Å) emission of the argon ion laser. When this ion is embedded in a properly chosen host, such as a tungstate or a molybdate, it will emit upon excitation a strong greenish-yellow color which has a peak at approximately 5440 Å.[7] The lifetime is approximately 0.5 msec, and the quantum efficiency is high, approaching 100%. We have examined the performance of $Na_{0.5}Tb_{0.5}WO_4$ under excitation by an argon laser (4880 Å) and find that 1-mm thick sample absorbs approximately 50% of the incident beam. This absorption cross section is substantially lower than optimum since a considerable thickness of material would be required to coat a display screen.

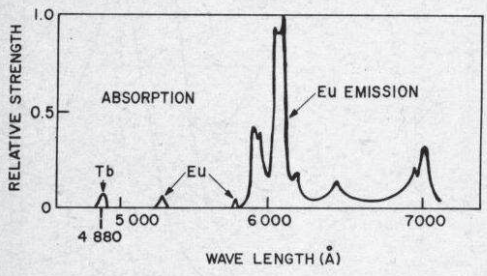

Fig. 1. Relative absorption spectra of Tb^{3+} and Eu^{3+} and the emission spectra of Eu^{3+}. When these two rare-earth ions are included in the same host, such as $Na_{0.5}Tb_{0.25}Eu_{0.25}WO_4$, absorption of argon laser radiation at 4880 Å is due to Tb^{3+} while excitation transfer to Eu^{3+} results in the characteristic Eu^{3+} emission spectrum which peaks in the red at 6140 Å.

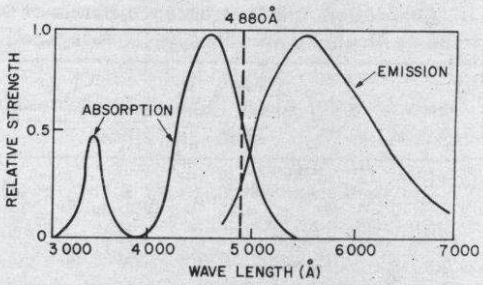

Fig. 2. Relative absorption and emission spectra of YAG:Ce. The broad absorption band is due to a *d*-band excitation.

It is possible to achieve other colors by photoluminescent conversion using different rare-earth ions. For example, Sm^{3+} has a peak emission at 5980 Å, Eu^{3+} at 6140 Å, Dy^{3+} at 5740 Å, and Er^{3+} at 5520 Å.[7] However, none of these transitions other than those for Tb^{3+} can be directly excited to any extent by the 4880-Å line of the argon laser. Generally, shorter wavelength excitation is required. However, indirect excitation of Eu^{3+} is possible through an intermediate Tb^{3+} ion.[8] For example, excitation transfer from Tb^{3+} to Eu^{3+} in $Na_{0.5}Tb_{0.25}Eu_{0.25}WO_4$ causes this material to emit a strong red color under 4880-Å illumination. The absorption bands of Tb^{3+} and Eu^{3+} and the emission of Eu^{3+} are displayed as a function of wavelength in Fig. 1. The absorption cross section, quantum efficiency, and lifetime of this material are similar to $Na_{0.5}Tb_{0.5}WO_4$ discussed above.

The Ce^{3+} and Eu^{2+} ions are exceptions to the general observation that the fluorescence of rare-earth ions is little affected by the host. This is so because their emissions are from *d*-bands which strongly interact with the crystal field.[9] A rather unusual but useful material is made by adding cerium to $Y_3Al_5O_{15}$ (YAG). The lower excited states of the crystal field components of the 5*d* configuration of the YAG:Ce composition are sufficiently low in energy that absorption of 4880-Å light becomes appreciable.[10] Figure 2 shows the absorption and emission spectra in detail. Note that the peak of the emission spectrum occurs at 5500 Å, the wavlength at which the eye is most sensitive. We have found that at 4880 Å the absorption cross section is approximately 30 dB/mm/wt % of Ce added to the YAG host. In addition to this relatively large absorption cross section, this compound has a very short lifetime of approximately 0.07 μsec (Ref. 11) and a quantum efficiency of approximately 70%.[10] These properties make YAG:Ce very attractive for display screen applications. Furthermore, this material may be *tuned* for a particular use. By replacing some Y with Gd the peaks of the absorption and emission spectra shift to somewhat longer wavelengths, while replacing Al with Ga causes the opposite effect.[10] Other Ce^{3+} and Eu^{2+} compositions that have been investigated[9,10] require excitation at wavelengths substantially shorter than 4880 Å, generally in the ultraviolet.[4]

In addition to the rare-earth compounds, there are large classes of inorganic phosphors which have II–VI hosts such as ZnS and activators such as Bi, Mn, Cu,

Table I. Absorption and Fluorescence Bands of Dyes in Aqueous or Alcoholic Solutions, after Pringsheim[15,a]

Compounds	First absorption band	Fluorescence	
		Band	Color
I. Xanthene			
Fluoran	uv	2900–4600 (3200)	violet strong
Fluorescein (Dihydroxyfluoran)	4400–5200 (4940)	5100–5900 (5180)	yellow-green very strong
Eosin (Tetrabromofluorescein)	4500–5600 (5170)	5200–6000 (5400)	yellow strong
Erythrosin (Tetraiodofluorescein)	4600–5560 5165	5180–5880 5375	yellow weak
Rose bengale (Tetraiodotetrachlorofluorescein)	(5438)	5500–6700 (6000)	orange very weak
Rhodamine B extra	4800–6000 (5500)	5500–7000 (6050)	red strong
Rhodamine 6G	4800–5900 (5260)	5360–6020 (5550)	yellow strong
Acridine red	4550–6000	5600–6800	orange medium
Pyronine B	5400–5900	5600–6500	orange medium
II. Acridine			
Acridine	3000–4500	4000–4800	blue-violet medium
Acridine yellow	uv–5200	4750–6400	green
Euchrysine	uv–5400	5050–6700 (5850)	greenish-yellow medium
Rheonine A	uv–5100	4700–6500	green weak
Acriflavine (Trypaflavine)	uv–5000	4850–6600	yellowish-green strong
III. Azine			
Magdala red	4000–6000 (5240)	5500–7000 (6000)	red strong
Safranine	(5390		yellow-red
IV. Thiazine			
Thionine	4800–6300 (5800)		orange medium
Methylene blue	5500–7000		red medium

[a] Approximate limits of bands in Å; peaks of bands in parentheses.

and Ag, and many activated tungstates, molybdates, vanadates, phosphates, germanates, and silicates that also have strong band fluorescence.[12] We have not found these materials to be particularly useful since most are not readily excited by argon radiation or are of inadequate quantum efficiency.

B. Organic Phosphors

There are a number of aromatic hydrocarbons and organic dyes that when properly treated exhibit strong fluorescence over a broad portion of the visible spectrum. Under white light illumination several of these appear to glow with a particular color ranging from greenish-yellow through orange to bright red. This dayglow phenomenon has found considerable use in advertising display and is due to strong absorption of blue and green light with subsequent emission at the various longer wavelengths.[13]

The fluorescing hydrocarbons and dyes are employed in very dilute form in order to achieve optimum quantum efficiency. Usually pigments (solid particles that carry dye) are formed by dissolving the dye in an organic resin solution which is subsequently condensed to an insoluble state by the application of heat.[14] In certain cases the efficiency is enhanced if the dye is adsorbed on colloids such as fibers or gel particles of high polymers.[14] Representative materials and the color which they fluoresce include pyrelene (blue), fluorescein (yellow-green), eosin (yellow), Rhodamine-B (red), Rhodamine-6G (yellow), acridine (blue), acriflavine (yellow-green), naphthalene red (red), Auromine-O (yellow-green), and 7-diethylamino-4 methyl coumarin (blue) as well as other xanthene, azine, oxazine, thioazine, acridine, flavin, naphthalimide, and coumarin derivatives. Additional data on the absorption and emission of selected dyes are given in Table I.[15]

We have examined in considerable detail a naphthalimide dye, 4-amino-1,8-naphthal-*p*-xenylimide (yellow-green), and two Rhodamine dyes (orange and red) that have been cast into an adhesive coated plastic film for commercial use (Minnesota Mining and Manufacturing Company, Scotchcal Fluorescent Film, types 3483, 3484, and 3485). Their emission spectra for 4880-Å excitation, which are shown in Fig. 3, exhibit peaks at 5200 Å (yellow-green), 6000 Å (orange), and 6200 Å (red). We have determined that their lifetimes are all considerably less than 1 μsec, and their absorption cross sections are so large that the entire laser beam is absorbed within the thin films which are approximately 0.1 mm thick. Their absorption bands are quite broad, including essentially all the violet and blue and a portion of the green. We have estimated from analysis of reflection spectra reported by Ward[16] that

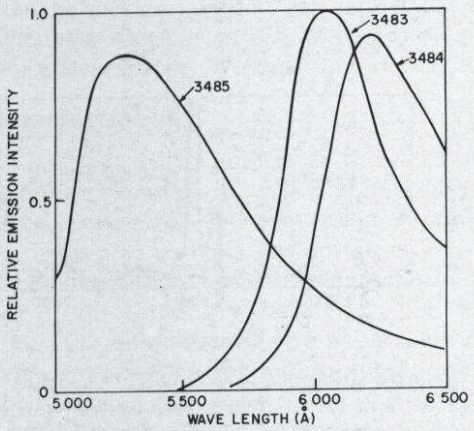

Fig. 3. Relative emission spectra of naphthalimide dye (3485) and Rhodamine dyes (3483 and 3484) due to excitation by the 4880-Å line of an argon laser.

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