Colored Emission of Rare Earth Ions in a Potassium Feldspar Glass

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The viability of rare earth ions as fluorescent coloring additives for dental porcelain was investigated. The data presented allow the formulation of porcelain with specific color properties under illumination by ultraviolet light. Attention is drawn to the possibility of energy transfer occurring with the result that prediction of color may not be done by application of the additive color-mixing scheme.

Lately there has been a resurgence of interest in the esthetic properties of dental porcelain. Various investigators have attempted to quantify and assess the fluorescent properties of uranium used as a fluorescent additive in dental porcelain.[1,2] In general, the behavior of porcelain and of denture teeth is not similar to that of natural teeth.

It has been known for some time that natural teeth show a pale blue color under illumination by ultraviolet light.[3,4] There have been no attempts to quantify this effect using vital teeth, though several studies have shown that the relative health of the teeth had some effect on the color.[5,6] Though some variance exists between individual teeth, fluorescent data indicate that the primary excitation wavelength is located at about 330 nm, while the emission peak is centered around 420 nm.[7]

Studies have been done on the porcelains used in crown and bridge work and denture teeth. A wide disparity was observed in the color revealed when specimens of these porcelains were irradiated by ultraviolet light.[8] Emission was found to occur at 395, 480, 520, and 580 nm[8] with the result that emission colors varied from blue to red.

One purpose of this study was to evaluate the fluorescent properties of rare earth ions in a glass with a composition similar to that of dental porcelain. The trivalent rare earth ions show strong colored fluorescence when exposed to ultraviolet light. With the exception of cerium, the electronic transitions responsible for colored light emission occur between various levels of the 4f electron configuration.[9] Interactions with the host material which are of great significance in the cases of transition metal ions and cerium are of minimal importance for the other trivalent rare earths, as the 4f electrons are shielded by outerlying valence electrons. Therefore, the energy gaps between the excited levels remain about the same, and emission peaks and emission color are relatively independent of the host.[10] For this reason, the trivalent rare earth ions may serve as useful fluorescent additives with a standard range of emission colors.

The host material chosen for this study was the chemical compound potassium feldspar: $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. This material served a twofold purpose: its composition was similar to that of dental porcelain, and second, its highly interconnected framework structure[11] (due to the lack of nonbridging oxygen ions) serves as a good host for the observation of energy transfer.

Materials and Methods

The starting materials used for the preparation of the glasses were aluminum hydroxide, silicon dioxide, and potassium carbonate hydrate. These materials were all reagent grade. The rare earth oxides used were PrO_2, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, and Tm_2O_3. They were phosphor grade, with a purity of at least 99.9%. The glasses contained either 0.5 mole percent of a single rare earth ion or the same amount of two dissimilar rare earth ions for a total of 1.0 mole
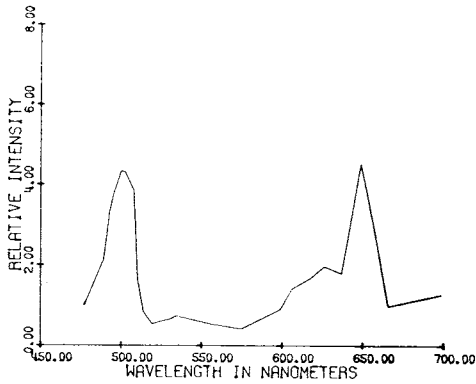
FIG 1.—Emission spectrum of 0.5 mole % Pr³⁺ in Potassium Feldspar glass with excitation wavelength = 440 nm.

percent. The amount of bridging oxygen ions in the glass was maintained by providing for a deficiency of potassium ions such that three moles of univalent potassium ions were withdrawn for one mole of trivalent rare earth ions added.

Prior to formulation, weight loss factors were determined for the aluminum hydroxide and potassium carbonate hydrate and appropriate corrections made during mass calculations. Appropriately weighed quantities of the host materials were ground under acetone and dried. They were then placed in platinum crucibles, calcined at 800 C for 8 hours and reground in an alumina mortar and pestle. The rare earth ions were added as nitrate solutions to the power and dried at 90 C and reground

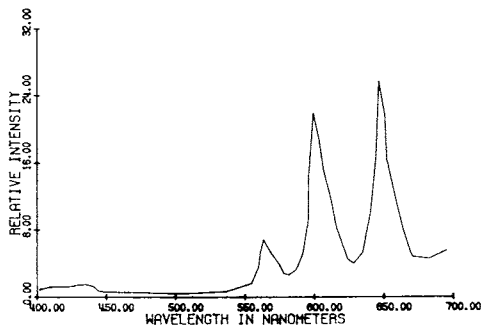* American Instrument Company, Silver Springs, Md.

FIG 2.—Emission spectrum of 0.5 mole % Sm³⁺ in Potassium Feldspar glass with excitation wavelength = 405 nm.

again. The dry powder was finally fused by an oxygen-natural gas flame with a pure silica rod used to support the molten mass. In this manner, solid glass samples were obtained for spectroscopy.

The instrument used for fluorescent analysis was a spectrophotofluorimeter.* The excitation source was a xenon lamp and the detector a photomultiplier tube with S-20 response characteristics. The resolution obtained with the proper selection of slit widths was 6 nm. Before analysis, the emission and excitation monochrometers were calibrated with a mercury lamp and a quinine sulfate standard solution, respectively.

Once fluorescent spectra were obtained, points along the spectrum curve were characterized by their "x" (wavelength) and "y"
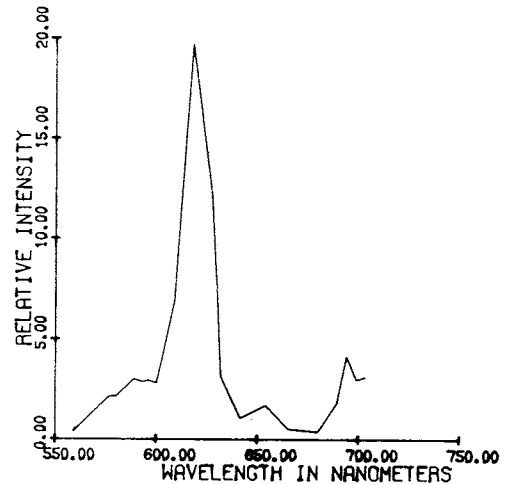

FIG 3.—Emission spectrum of 0.5 mole % Eu³⁺ in Potassium Feldspar glass with excitation wavelength = 395 nm.

(relative intensity) coordinates and stored on computer cards. These digital data were then treated by a computer programmed to correct the relative intensity values for instrument response variability. Another function of the computer was to calculate tristimulus values and chromaticity coordinates that would quantitatively characterize the color of the fluorescent emission. The procedure used has been documented by Wyszecki[12] and consisted of integrating the area under the spectrum curve between two successive wavelength values, multiplying by the color-matching functions

documented in the 1931 C.I.E. table and sum-mation of the products to give tristimulus values. The chromaticity coordinates were then obtained as relative values from the tristimulus values and may be used to name the color on the chromaticity diagram as suggested by Kelly.[13]

Results

SINGLY ACTIVATED GLASSES.—Emission spectra of glasses activated with Pr^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Tm^{3+} are presented in Figures 1 through 8. The excitation wavelengths used were those which caused the most intense emission, though other excitation wavelengths may be used, as those documented in Table 1. The computer gen-erated tristimulus values are presented in Table 2.
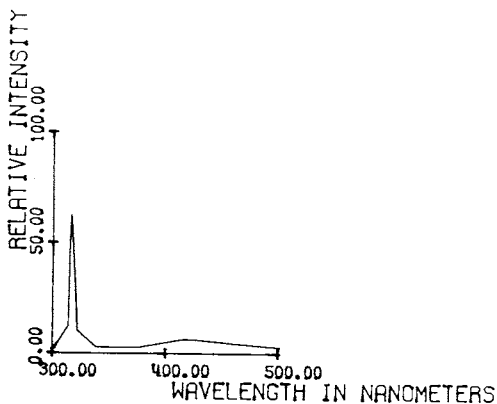

FIG 4.—Emission spectrum of 0.5 mole % Gd^{3+} in Potassium Feldspar glass with excitation wavelength = 275 nm.

DOUBLY ACTIVATED GLASSES.—The emis-sion spectra of samples activated by two dis-similar rare earth species are notable in some cases due to the presence of energy transfer between the dissimilar ions. Energy transfer may cause the appearance of peaks not found in the emission spectra when either one of the rare earths is used to activate the glass, as shown in Figure 9, which illustrates the emis-sion spectrum of a glass containing Dy^{3+} and Sm^{3+}.

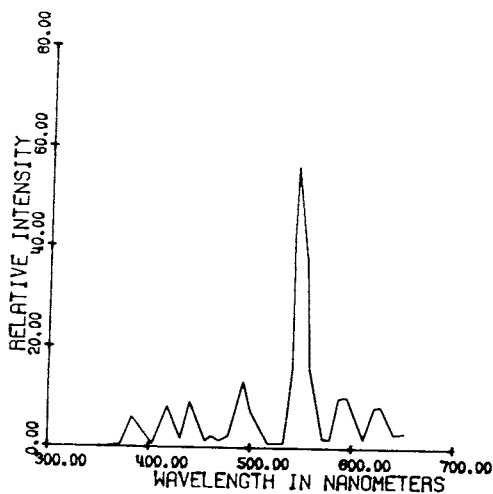Energy transfer may also be responsible for the disappearance of peaks normally pres-

FIG 5.—Emission spectrum of 0.5 mole % Tb^{3+} in Potassium Feldspar glass with excitation wavelength = 225 nm.

ent, as shown in Figure 10, which represents the emission spectrum of a glass containing Dy^{3+} and Nd^{3+}. Comparison of this spectrum with that shown in Figure 6, of a glass with Dy^{3+} alone, shows a considerable decrease in Dy^{3+} fluorescent intensity.

Discussion

The data presented for samples contain-ing single species of rare earths indicate im-mediately both the color and the intensity of that color. The color name itself is denoted
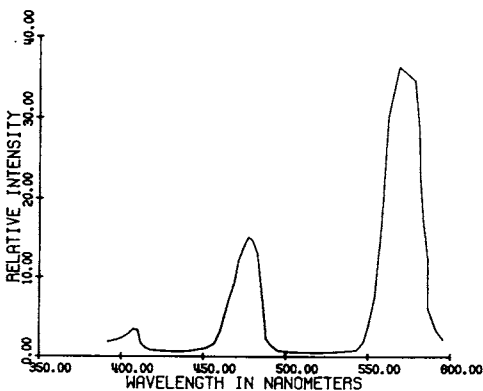

FIG 6.—Emission spectrum of 0.5 mole % Dy^{3+} in Potassium Feldspar glass with excitation wavelength = 352 nm.
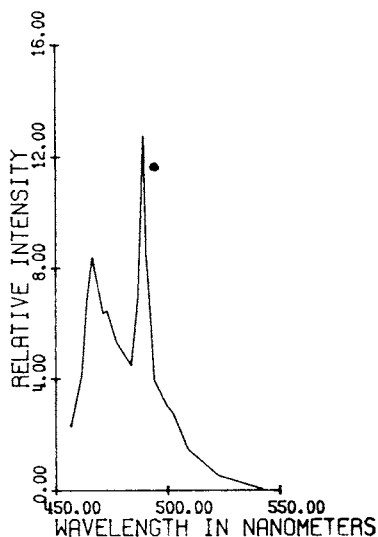
FIG 7.—Emission spectrum of 0.5 mole % Ho^{3+} in Potassium Feldspar glass with excitation wavelength = 442 nm.
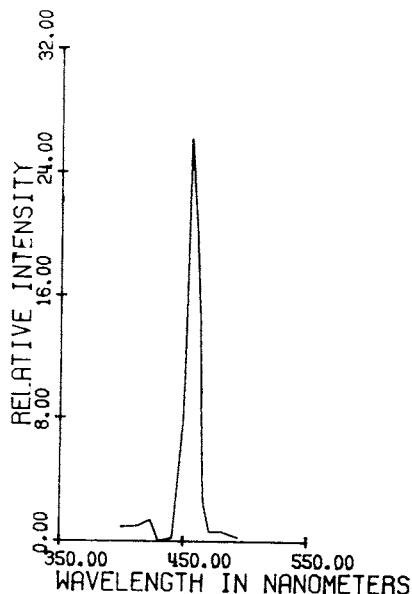

FIG 8.—Emission spectrum of 0.5 mole % Tm^{3+} in Potassium Feldspar glass with excitation wavelength = 360 nm.

TABLE 1

PRIMARY EXCITATION AND EMISSION WAVELENGTHS OF
RARE EARTH IONS IN POTASSIUM FELDSPAR GLASS

Ion	Excitation Wavelengths (nm)	Emission Wavelengths (nm)
Pr^{3+}	440	503, 535, 627, 650
Sm^{3+}	345, 362, 375, 405, 417	467, 565, 600, 650
Eu^{3+}	250, 330, 363, 383, 395, 413	575, 580, 583, 615, 652, 692, 702
Gd^{3+}	252, 275	317
Tb^{3+}	225, 260, 315, 350, 365, 375	385, 417, 440, 460, 490, 545, 590, 625
Dy^{3+}	325, 352, 365, 390, 425, 455	405, 475, 580
Ho^{3+}	412, 442	464, 475, 492, 505
Tm^{3+}	265, 295, 360, 400	425, 455

TABLE 2

COLOR PROPERTIES OF RARE EARTH ION FLUORESCENT EMISSION

Ion	Excitation (nm)	Tristimulus Values*			Chromaticity Coordinates			Color†
		R	G	B	X	Y	Z	
Pr^{3+}	440	.092	.103	.028	.415	.461	.123	gY
Sm^{3+}	405	1.	.627	.036	.601	.376	.02	R
Eu^{3+}	395	.312	.168	0	.649	.35	.0	rO
Tb^{3+}	225	.648	.908	.354	.339	.475	.185	yG
Dy^{3+}	352	.598	.709	.284	.375	.445	.178	YG
Ho^{3+}	442	.025	.043	.179	.103	.174	.722	B
Tm^{3+}	360	.077	.018	.430	.147	.034	.818	pB
$Dy^{3+} + Nd^{3+}$	352	.044	.035	.082	.273	.219	.507	S
$Dy^{3+} + Sm^{3+}$	405	.627	.412	.072	.564	.370	.064	rO

* These values have been normalized and indicate the relative intensity of the primary color (R = red, G = green, B = blue).
† From Kelly[13]. Upper case letters indicate a high chroma; lower case letters a low chroma, with Y = yellow, P = purple, O = orange, R = red, G = green, B = blue, S = source.

by chromaticity coordinates. The intensity of that color may be appreciated by a comparison of tristimulus values. These values were originally generated by the computer, then normalized so that direct comparison may be made between the various samples.

Although the spectra were obtained using monochromatic excitation radiation, the results are comparable to those which would be obtained under broad band excitation such as is supplied by a laboratory ultraviolet lamp or sunlight. Natural sunlight has a distinct ultraviolet component extending to 290 nm. The maximum intensity of this component occurs
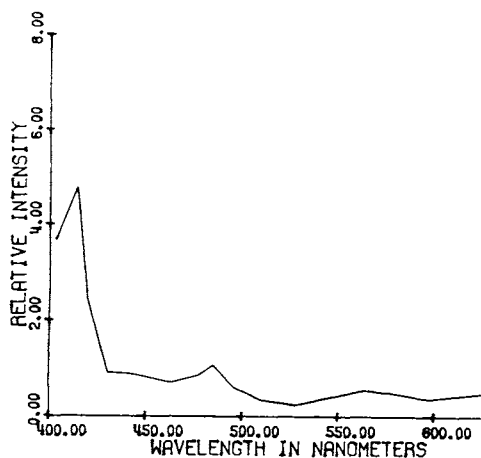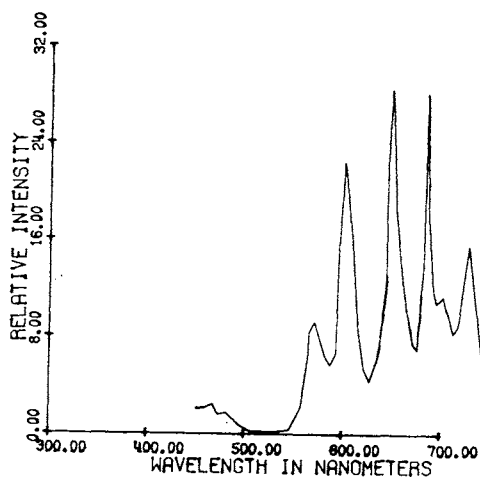

FIG 10.—Emission spectrum of 0.5 mole % Dy^{3+} and 0.5 mole % Sm^{3+} in Potassium Feldspar glass with excitation wavelength = 405 nm.

transfer. There is a notable decrease in the intensities of the emission peaks at 480 and 575 nm. The effect is due to the presence of Nd^{3+} absorption at these wavelengths.[15] Therefore, although Dy^{3+} is emitting radiation, this emission is absorbed by Nd^{3+}, causing excitation of the Nd^{3+} ions, which

FIG 9.—Emission spectrum of 0.5 mole % Dy^{3+} and 0.5 mole % Nd^{3+} in Potassium Feldspar glass with excitation wavelength = 352 nm.

at 370 nm.[14] Laboratory ultraviolet lamps of the long wavelength variety also have their highest output at 360 nm. Therefore, the ions Dy^{3+} and Tm^{3+} will exhibit the same emission color in sunlight and under laboratory ultraviolet lamps as given in Table 2, since the primary excitation wavelengths used in this analysis for these ions are so close to the wavelengths of the ultraviolet light found in the two sources. In the cases of the other ions, the colors may vary slightly in shade, though not enough to completely change the hue (i.e., red to yellow, etc.). Table 3 gives the colors observed by the naked eye when the samples were excited by a laboratory ultraviolet lamp.

The sample containing equal amounts of Dy^{3+} and Nd^{3+} shows the presence of energy
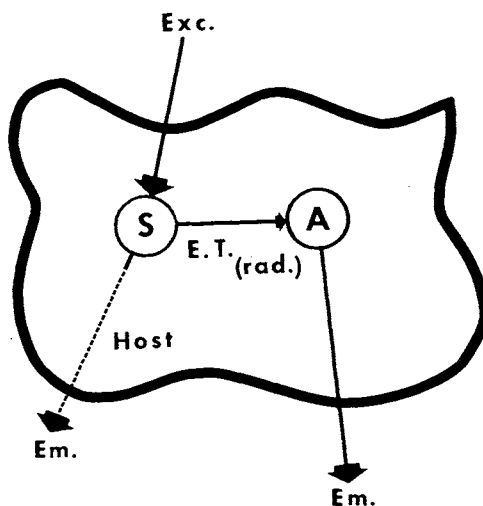

FIG 11.—Mechanism of radiative energy transfer. The excitation radiation absorbed by the sensitizer ion (S) is transferred radiatively to the activator ion (A). The activator ion then emits radiation, and in some cases, if not all energy is transferred, the sensitizer will also emit radiation.

TABLE 3

COLORED EMISSION OF RARE EARTHS UNDER
EXITATION BY A LABORATORY ULTRAVIOLET
LAMP (360 nm)

Ion	Observed Color
Pr^{3+}	*
Sm^{3+}	red-orange
Eu^{3+}	pink
Tb^{3+}	yellow-green
Dy^{3+}	yellow
Ho^{3+}	*
Tm^{3+}	purple
$Dy^{3+} + Nd^{3+}$	*
$Dy^{3+} + Sm^{3+}$	orange

* Fluorescence too faint to detect color with naked eye.

themselves emit radiation in the infrared portion of the spectrum. The energy transfer occurring between Dy^{3+} and Nd^{3+} is termed "radiative." The mechanism is portrayed in Figure 11. Excitation radiation absorbed by the sensitizer ion "S" (in this case Dy^{3+}) is transferred via emitted radiation to the activator ion "A" (in this case Nd^{3+}). In some cases, not all the energy is transferred and the sensitizer and activator ions will emit. Accordingly, due to energy transfer, the color values

for this sample, even though no new visible emission occurs, will be different from those calculated when Dy^{3+} alone is used.

The presence of energy transfer is also evident in the sample containing both Dy^{3+} and Sm^{3+}. In this case, interactions between the two ions cause the appearance of new peaks at 683, 702, and 730 nm. The energy transfer occurring in this case is termed "non-radiative." The mechanism of the transfer is portrayed in Figure 12. The energy absorbed by the sensitizer ion is transferred by phonons to the activator ion. Depending on the probability of transfer, all or some of the energy may be transferred, so that both ions may emit. Again, as a result of energy transfer, the color points will change.

The possibility of energy transfer must be taken into account when attempting to predict the color of emission when two dissimilar rare earth ions are both present in a host. If no interactions occur between the rare earth ions, the resulting color may be predicted using the color mixing scheme. In this case, the emission of both ions would occur simultaneously and independently. This is shown schematically in Figure 13. Both the sensitizer and activator ions are excited and both emit in their normal manner. The additive color mixing scheme may not apply in cases where energy transfer
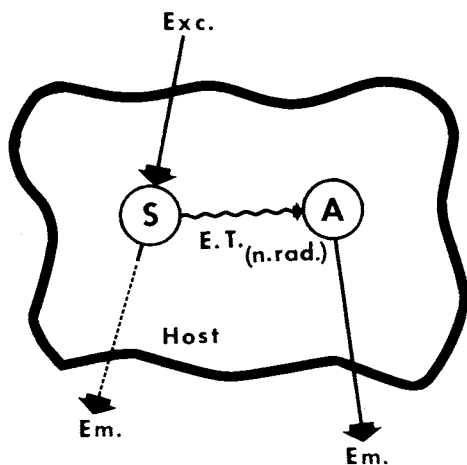

FIG 12.—Mechanism of nonradiative energy transfer. The excitation radiation absorbed by the sensitizer ion (S) is transferred by means of phonons to the activator ion (A). The activator then emits radiation, and in some cases, if not all energy is transferred, the sensitizer will also emit radiation.
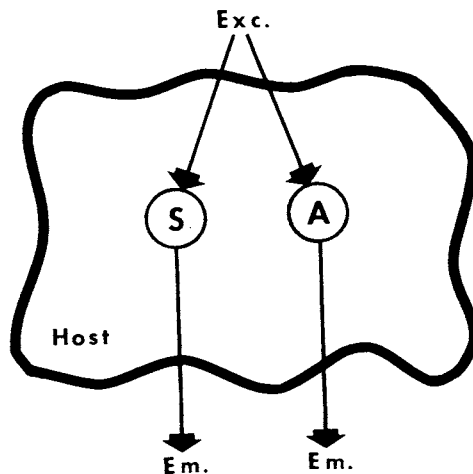

FIG 13.—Behavior of dissimilar ions when no energy transfer occurs and the additive color mixing scheme applies. The excitation radiation is absorbed by both sensitizer (S) and activator (A) ions which both emit radiation independently of one another.

occurs, as the interactions cause the ordinary pattern of emissions to change. The possibility of radiative energy transfer may be suspected if an ion has an emission peak at the same wavelength that another ion, present in the same host, has an absorption or excitation peak at the same wavelength. For example, the emission of Gd^{3+} at 310 nm will be absorbed by the Tb^{3+} ion causing a transfer of energy from Gd^{3+} to Tb^{3+}. Another example is the case of a host containing both Dy^{3+} and Tm^{3+}, where Tm^{3+} emission at 455 mm may be used to excite the Dy^{3+} ion.

Conclusions

It has been shown that rare earth ions may serve as fluorescent color additives in a glass with a composition similar to that of dental porcelain. The data presented allow for the identification of fluorescent additives currently used in most dental ceramics. The color values calculated from the emission spectra will also permit formulation of porcelains with desirable fluorescent emission properties, and a scheme for detection of possible energy transfer phenomena has been found to apply in at least one instance.

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