# Spectral Emission Properties of NBS Standard Phosphor Samples Under Photo-Excitation 


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#### Abstract

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.


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# SPECTRAL EMISSION PROPERTIES OF NBS STANDARD PHOSPHOR SAMPLES UNDER PHOTO-EXCITATION 

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The photo-excitation spectral emission properties of 10 of the 14 NBS standard phosphor samples have been determined. Pressed tablets of the phosphors were excited by radiation from a mercury arc lamp, passing through a narrow band-pass filter to obtain either $2537 \AA$ or $3650 \AA$ excitation. The measurement system is described, correction of the data is discussed, and the spectral emission data are presented. Relative quantum efficiencies were calculated. The results are compared with measurements reported by two other laboratories.

Key Words: Phosphors, photo-excitation, photoluminescence, spectral emission, spectral radiometry, standard phosphor samples.

## 1. Int roduction

The spectral emission properties of ten NBS standard phosphor samples under ultraviolet excitation have been measured. The phosphors and the exciting radiation used are listed in Table I. The relative quantum efficiencies of the $2537 \AA$ excited phosphors were calculated relative to magnesium tungstate from the data obtained.

The purpose of this report is to describe the measurement technique used, to discuss a computer program written to reduce the raw data, and to present the results obtained.
2. Measurement Technique

Measurements of the relative spectral emission of the phosphor samples under photo-excitation were made with the equipment shown in Figure 1. The phosphor powder sample to be measured was placed in a small cup made of aluminum ( 1.25 inches in diameter and approximately 0.04 inch deep) and pressed level by using a spatula. This phosphor plaque was then placed on a turret sample holder mounted horizontally in front of the monochromator which was mounted vertically.

A 4-watt low-pressure mercury-arc lamp (germicidal) was used as source for $2537 \AA$ excitation with a filter (Corning No. 9863) in front of the 1 amp to block the mercury lines in the visible region. A 100-watt high-pressure mercury-arc lamp with a narrow-band-pass filter centered at $3650 \AA$, in front

[^1]TABLE I

| $\begin{gathered} \text { Sample } \\ \text { No. } \\ \hline \end{gathered}$ | NBS Standard Sample Phosphors |  | Use |
| :---: | :---: | :---: | :---: |
|  | Excitation ( $\AA$ ) | Phosphor Description |  |
| 1020 | 3650 | Zinc Sulfide <br> ZnS:Ag | Blue Component of P-4 Cathode Ray Tube (CRT) Phosphor |
| 1021 | 2537 | Zinc Silicate $\mathrm{Zn}_{2} \mathrm{SiO}_{4}: \mathrm{Mn}$ | P-1 CRT Phosphor |
| 1022 | 3650 | Zinc Sulfide $\mathrm{ZnS}: \mathrm{Cu}$ | P-2 CRT Phosphor |
| 1023 | 3650 | $\begin{aligned} & \text { Zinc-Cadmium Sulfide } \\ & \text { ZnCdS:Ag } \end{aligned}$ | Yellow Component of P-4 CRT Phosphor |
| 1024 | 3650 | $\begin{aligned} & \text { Zinc-Cadmium Sulfide } \\ & \text { ZnCdS:Cu } \end{aligned}$ | Orange Component of P-14 CRT Phosphor |
| 1025 | ---- (1) | Zinc Phosphate $\mathrm{Zn}_{3}\left(\mathrm{PO}_{4}\right)_{2}: \mathrm{Mn}$ | Red Component of P-22 CRT Phosphor |
| 1026 | 2537 | Calcium Tungstate $\mathrm{CaWO}_{4}: \mathrm{Pb}$ | CRT, Lamps |
| 1027 | 2537 | Magnesium Tungstate $\mathrm{MgWO}_{4}$ | CRT, Lamps |
| 1028 | 2537 | Zinc Silicate $\mathrm{Zn}_{2} \mathrm{SiO}_{4}: \mathrm{Mn}$ | Lamps |
| 1029 | 2537 | Calcium Silicate $\mathrm{CaSiO}_{3}: \mathrm{Pb}, \mathrm{Mn}$ | Lamps |
| 1030 | ----(2) | Magnesium Arsenate $(\mathrm{MgO})_{\mathrm{x}}\left(\mathrm{As}_{2} \mathrm{O}_{5}\right)_{\mathrm{y}}: \mathrm{Mn}$ | Lamps |
| 1031 | 2537 | Calcium Halophosphate $3 \mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right) \cdot \mathrm{Ca}(\mathrm{F}, \mathrm{Cl}): \mathrm{Sb} ; \mathrm{Mn}$ | Lamps |
| 1032 | ----(3) | Barium Silicate $\mathrm{BaS}_{2} \mathrm{O}_{5}: \mathrm{Pb}$ | Lamps (UV) |
| 1033 | ----(3) | Calcium Phosphate $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}: \mathrm{Tl}$ | Lamps (UV) |

(1) Would not emit under $2537 \AA$ or $3650 \AA$ excitation
(2) Fine emission structure not resolved with $5 \AA$ pass band of monochromator used; results not reported
(3) Not measured.
of the 1 amp , was used as a source of $3650 \AA$ excitation. The output of the monochromator was measured by using a photomultiplier tube (PMT) with an S-20 photocathode (Dumont EM2433), an amplifier or a picoammeter, and a digital voltmeter as shown in Figure 1.


## Figure 1 Spectral Measurement Equipment

In order to calibrate the monochromator and PMT combination, its relative spectral sensitivity was measured by using an NBS color temperature standard operated at a color temperature of 2854 K . A USP grade barium sulfate (standard reflector) plaque was placed on the turret sample holder so that it could be rotated into position in front of the entrance slit of the monochromator. The spectral radiant flux of the color temperature standard, as diffusely reflected by the plaque, was used to calibrate the equipment.

A measurement of the phosphor sample consisted of setting the monochromator at a particular wavelength (scale readable to three places), and recording the digital voltage reading; first, with the color temperature lamp and the $\mathrm{BaSO}_{4}$ plaque; and second, with the excitation source and the phosphor sample in front of the entrance slit. Both lamps were housed and shuttered such that they could be left on continuously during a data run and used independently. The wavelength scale on the monochromator was verified by using the mercury lines in the low pressure excitation source.

## 3. Computer Correction of Data

A computer program was used to calculate the relative spectral sensitivity of the instrument for each run and to apply calibration corrections to the data obtained in order to obtain the relative spectral distribution of the phosphor photo-luminescence for each data run. The corrected phosphor relative radiant energy distribution curves for several independent runs were then averaged over the number of runs to provide an average curve for each phosphor measured.

The following quantities are defined:
N $\quad \equiv$ Number of data runs for each phosphor
$\lambda_{j} \quad \equiv$ Wavelength value: $j=1, \ldots, 20$
$S_{i}\left(\lambda_{j}\right) \equiv \begin{aligned} & \text { Relative sensitivity of instrument for the } i-t h \text { data run } \\ & \\ & i=1, \ldots, N\end{aligned}$
$C_{i}\left(\lambda_{j}\right) \equiv$ Digital voltage reading when using color temperature lamp and $\mathrm{BaSO}_{4}$ plaque for the $i-t h$ data run at the $j$-th wavelength value
$\mathrm{L}\left(\lambda_{\mathbf{j}}\right) \equiv$ Relative spectral luminance of $\mathrm{BaSO}_{4}$ plaque when irradiated by color temperature standard (2854K).
$\begin{aligned} & D_{i}\left(\lambda_{j}\right) \equiv \text { Digital voltage reading when using excitation source and } \\ & \text { phosphor plaque. }\end{aligned}$
Thus, since $C_{1}\left(\lambda_{j}\right)$ is by definition

$$
\begin{equation*}
C_{1}\left(\lambda_{j}\right)=S_{i}\left(\lambda_{j}\right) L\left(\lambda_{j}\right), \tag{1}
\end{equation*}
$$

the relative spectral sensitivity for the i-th data run is therefore

$$
\begin{equation*}
S_{i}\left(\lambda_{j}\right)=\frac{C_{i}\left(\lambda_{j}\right)}{L\left(\lambda_{j}\right)} \tag{2}
\end{equation*}
$$

also by definition,

$$
\begin{equation*}
D_{i}\left(\lambda_{j}\right)=S_{i}\left(\lambda_{j}\right) P_{i}\left(\lambda_{j}\right) \tag{3}
\end{equation*}
$$

where:
$P_{i}\left(\lambda_{j}\right) \equiv \begin{aligned} & \text { Relative radiant energy distribution of the phosphor for } i-t h\end{aligned}$
Therefore,

$$
\begin{equation*}
P_{i}\left(\lambda_{j}\right)=\frac{D_{i}\left(\lambda_{i}\right)}{S_{i}\left(\lambda_{j}\right)}=\frac{D_{i}\left(\lambda_{j}\right) L\left(\lambda_{j}\right)}{C_{i}\left(\lambda_{j}\right)} \tag{4}
\end{equation*}
$$

and the normalized distribution curve is given by,

$$
\begin{equation*}
N P_{i}\left(\lambda_{j}\right)=\frac{P_{i}\left(\lambda_{j}\right)}{P_{i_{M a x}}} \tag{5}
\end{equation*}
$$

where:

$$
P_{i_{M a x}} \equiv \text { Maximum value of } P_{i}\left(\lambda_{j}\right) \text { for } j=1, \ldots, 20
$$

and the average relative energy distribution over the $N$ data runs for each phosphor is finally

$$
P_{\text {ave }}\left(\lambda_{j}\right)=\frac{\sum_{i=1}^{N} N P_{i}\left(\lambda_{j}\right)}{N}
$$

The relative energy distribution curves obtained for the ten phosphors measured are shown in figures 2 to 11. Each figure is followed by its computer output data, in Tables 2 to 11 , showing the tabular values for each curve. The average curve for each phosphor is plotted and the tabular values are given on each curve. The tabular values shown are $95 \%$ confidence interval estimates of the true mean, calculated as:

$$
\bar{x} \pm \tau_{n} w
$$

where: $\quad w=$ range (maximum value minus minimum value)
n = sample size
$\overline{\mathrm{x}}=$ computed mean of sample
and values of $\tau_{n}$ are given in Table $8 c(1)$, page 408, of Ref. 5 .
The relative energy distribution curves obtained for Sample Nos. 1020, 1022, 1023 and 1024 with photo-excitation are compared with data obtained with cathode-ray excitation by Bril (Ref. 2). Sample 1022 is a P-2 phosphor and the JEDEC $\mathrm{P}-2$ data (Ref 3) is compared with the results obtained with photo-excitation.

The relative energy distribution curves obtained for Sample Nos. 1021 and 1026 with 2537 A excitation are, compared with results obtained by Bril (Ref 1) also with 2537 A excitation. While Sample No. 1021 compares very closely with Bril's data, Sample No. 1026 shows some differences. Sample Nos. 1026 and 1029 have been compared with data obtained in 1961 by Dr. Frank J. Studer at the Nela Park Laboratory of the General Electric Company (now at NBS). The two sets of data are in close agreement. Since Sample No. 1021 is a P-1 phosphor, the JEDEC P-1 curve is also plotted from Ref. 3.

The difference shown in comparing the results obtained with photo- and cathode-ray excitation are the same order of magnitude as the differences noted above obtained for Sample No. 1026 from data obtained with only photoexcitation, e.g., compare results for Sample No. 1024 where the results of photo and cathode ray excitation are shown, with Sample No. 1026. One might therefore hypothesize that the spectral emission curves are independent of the excitation used, but this hypothesis requires further investigation.

The tabular results show the repeatability of the measurements. In general, the results obtained with the low-pressure mercury-arc lamp (2537 $\AA$ excitation) are more repeatable than those obtained with the high-pressure lamp ( 3650 excitation) because of greater fluctuations of the output of the latter lamp.

Other measurement problems and sources of uncertainty include the low resolution of the wavelength scale on the monochromator (readable to only three places), the incomplete blocking of the mercury lines by the filter (preventing accurate readings near 4000 \& with 2537 A excitation source), and the variations in the physical repositioning of the sample with the turret mount between data points.

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| WAVE LENGTH |  | **NORMALI ZED CURVES** |  |  |  |  |  | A VERAGE |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3800 | 0.007 | 0.0 Cb | 0.007 - | 0.006 | 0.006 | 0.006 | 0.006 | 0.006 |
| 390C | 0.011 | 0.010 | 0.011 | 0.012 | 0.012 | 0.012 | 0.012 | 0.011 |
| 4000 | 0.044 | 0.045 | 0.047 | 0.050 | 0.050 | 0.050 | 0.050 | 0.048 |
| 4100 | 0.162 | 0.164 | 0.163 | 0.172 | 0.170 | 0.171 | 0.168 | 0.167 |
| 420 C | 0.399 | 0.402 | 0.395 | 0.405 | 0.412 | 0.410 | 0.406 | 0.404 |
| 4300 | 0.703 | 0.690 | 0.699 | 0.707 | 0.713 | 0.713 | 0.705 | 0.704 |
| 4400 | 0.935 | 0.936 | 0.936 | 0.940 | 0.940 | 0.941 | 0.938 | 0.938 |
| 450 C | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 460 C | 0.897 | 0.897 | 0.899 | 0.897 | 0.907 | 0.899 | 0.899 | 0.899 |
| $\checkmark 4700$ | $0.7 C 4$ | 0.438 | 0.709 | 0.699 | 0.687 | 0.694 | 0.695 | 0.661 |
| 4800 | 0.491 | 0.296 | 0.490 | 0.489 | 0.496 | 0.506 | 0.498 | 0.467 |
| 4900 | 0.329 | 0.1 .58 | 0.334 | 0.325 | 0.336 | 0.331 | 0.332 | 0.306 |
| 5 COC | 0.211 | 0.112 | 0.209 | 0.206 | 0.208 | 0.209 | 0.208 | 0.195 |
| 510 C | 0.124 | 0.075 | 0.130 | 0.129 | 0.119 | 0.129 | 0.130 | 0.119 |
| 5200 | 0.076 | 0.044 | 0.086 | 0.080 | 0.079 | 0.079 | 0.079 | 0.075 |
| 5300 | 0.048 | 0.038 | 0.051 | 0.048 | 0.049 | 0.049 | 0.050 | 0.048 |



| WAVE LENGTH |  | **NORMALI ZED CURVES** |  |  |  |  |  |  | A VERAGE |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4900 | 0.100 | 0.098 | 0.097 | 0.102 | 0.104 | 0.099 | 0.087 | 0.105 | 0.099 |
| 4950 | 0.200 | 0.203 | 0.200 | 0.204 | 0.198 | 0.198 | 0.193 | 0.202 | 0.200 |
| 5000 | 0.347 | 0.342 | 0.329 | 0.342 | 0.345 | 0.333 | 0.332 | 0.349 | 0.340 |
| 505 C | 0.498 | 0.515 | 0.504 | 0.515 | 0.526 | 0.514 | 0.513 | 0.515 | 0.512 |
| 510 C | 0.720 | 0.709 | 0.696 | 0.711 | 0.729 | 0.707 | 0.710 | 0.725 | 0.714 |
| 5150 | 0.890 | 0.899 | 0.884 | 0.900 | 0.899 | 0.892 | 0.898 | 0.901 | 0.895 |
| 5200 | 1.000 | 0.558 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 5250 | 0.994 | 1.000 | 0.982 | 0.991 | 0.998 | 0.994 | 0.994 | 0.993 | 0.993 |
| 5300 | 0.916 | 0.931 | 0.963 | 0.918 | 0.927 | 0.934 | 0.909 | 0.910 | 0.918 |
| 5350 | 0.793 | 0.805 | 0.772 | 0.787 | 0.789 | 0.805 | 0.774 | 0.779 | 0.788 |
| 5400 | 0.647 | 0.663 | 0.644 | 0.655 | 0.6 .53 | 0.670 | 0.644 | 0.646 | 0.653 |
| 545 C | 0.521 | 0.525 | 0.518 | 0.526 | 0.532 | 0.524 | 0.504 | 0.510 | 0.520 |
| 5500 | 0.398 | 0.469 | 0.388 | 0.400 | 0.418 | 0.415 | 0.367 | 0.399 | 0.399 |
| 5550 | 0.3 C 8 | 0.312 | 0.303 | 0.310 | 0.317 | 0.315 | 0.298 | 0.307 | 0.309 |
| 5600 | 0.230 | 0.231 | 0.230 | 0.233 | 0.238 | 0.236 | 0.218 | 0.230 | 0.231 |
| $565 C$ | 0.174 | 0.176 | 0.171 | 0.178 | 0.175 | 0.174 | 0.160 | 0.167 | 0.172 |
| 5700 | 0.133 | 0.121 | 0.125 | 0.130 | 0.132 | 0.132 | 0.118 | 0.121 | 0.128 |
| 5750 | 0.094 | 0.094 | 0.094 | 0.098 | 0.100 | 0.091 | 0.092 | 0.092 | 0.095 |
| 580 C | 0.073 | 0.071 | 0.067 | 0.070 | 0.072 | 0.071 | 0.068 | 0.066 | 0.070 |
| 585 C | 0.052 | 0.054 | 0.055 | 0.056 | 0.057 | 0.057 | 0.049 | 0.053 | 0.054 |






\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline \multirow[t]{10}{*}{1.0} \& \& H1I \& \& \& \& \& \& \& \& \& \& \& \& \& \& \& \& 1: \& \& \& \& \& \& \& \& \&  \& \& \& \& \& \& \& \& \& \& \& \& \& \# \& \& \& 7 <br>
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The $45^{\circ}-0^{\circ}$ spectral reflectance factor of the $\mathrm{BaSO}_{4}$ plaque was assumed constant over the wavelength range of interest for each phosphor and the relative spectral emission for a blackbody at $2854^{\circ} \mathrm{K}$ was used for $L\left(\lambda_{\text {i }}\right)$ in all calculations involved in correcting the data. The absolute spectral reflectance of USP grade (unpublished data) $\mathrm{BaSO}_{4}$ is shown in Figure 12. The $45^{\circ}-0^{\circ}$ spectral reflectance factor of the plaque was assumed to be equal to its spectral reflectance.

## 4. Relative Quantum Efficiency

The relative quantum efficiencies of the 2537 A excited phosphor samples have been calculated from the scale factors used with a picoammeter during the measurements. The method of calculation is as follows: define

$$
f \equiv \text { scale factor }
$$

then the calibrated spectral energy distribution is

$$
E(\lambda)=f P(\lambda)
$$

where $P(\lambda)$ is the average curve obtained for each phosphor. Thus, since

$$
E=h v=\frac{h c}{\lambda}
$$

the number of quanta of luminescence is given by,

$$
Q=f \int \frac{P(\lambda)}{\frac{h c}{\lambda}} d \lambda=\frac{f}{h c} \int \lambda P(\lambda) d \lambda .
$$

Since the calculated quantum efficiencies of the samples will be referred to $\mathrm{MgWO}_{4}$, we compute the number of quanta emitted by it as

$$
\mathrm{Q}_{\mathrm{MgWO}_{4}}=\frac{\mathrm{f}_{\mathrm{MgWO}_{4}}}{\mathrm{hc}} \int \lambda \mathrm{P}_{\mathrm{MgWO}_{4}}(\lambda) \mathrm{d} \lambda
$$

Finally the relative quantum efficiency of each sample is given by,

$$
\epsilon \equiv \operatorname{Rel} \text { ative } Q . E .=\frac{Q}{Q_{\mathrm{MgWO}_{4}}}=\frac{f \int \lambda P(\lambda) d \lambda}{f_{\mathrm{MgWO}_{4}} \int \lambda P(\lambda) \mathrm{d} \lambda}
$$

or for ease of calculation from the data,

$$
\varepsilon=\frac{f_{j=1}^{20} \lambda_{j} P\left(\lambda_{j}\right)}{f_{\mathrm{MgWO}_{4}} \sum_{j=1}^{20} \lambda_{j} P\left(\lambda_{j}\right)}
$$



The following results were obtained with the quantum efficiency of $\mathrm{MgWO}_{4}$ normalized to unity.

RELATIVE QUANTUM EFFICIENCIES
OF $2537 \AA$ EXCITED SAMPLES

| Sample No. | $\epsilon$ | Per Bril (Ref 1) |
| :--- | ---: | :---: |
| 1021 | .66 | .83 |
| 1026 | .86 | .89 |
| $1027\left(\mathrm{M}_{\left.\mathrm{g} \mathrm{WO}_{4}\right)}\right.$ | 1.00 | 1.00 |
| 1028 | .86 | .81 |
| 1029 | .85 | .81 |
| 1031 | .82 | .84 |

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