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CURRENT-SENSITIVE SINGLE-GUN COLOR CATHODE RAY TUBE

By F. J. Avella

June 1970

Prepared under Contract No. NAS 12-2188 by
GENERAL TELEPHONE & ELECTRONICS LABORATORIES INCORPORATED
Bayside, New York

Electronics Research Center
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

This program has extended earlier investigations in the use of nonlinear phosphors to produce current-sensitive color CRT screens. A survey of the emission linearity of a large number of experimental phosphors resulted in finding two improved green-emitting sublinear phosphors. The preparation parameters necessary to obtain nonlinear phosphors reproducibly were optimized.

Several single-component phosphors which gave a spectral shift with variations in current density were synthesized and evaluated. The effects of several types of absorption filters on color gamut and contrast were also examined for use with the spectral shift phosphors as well as for mixed phosphor blends.

Several experimental CRTs were fabricated and evaluated, and three deliveries of sample tubes were made representing different types of phosphor screens to give current sensitive color shifts.

Work on this project was performed during the period from July 1, 1969 to June 30, 1970 for the NASA-Electronics Research Center in Cambridge, Mass. with Mr. Hans Bullinger as the technical monitor. Principal investigator of the GT&E Laboratories, Bayside Research Center, was Mr. Frank J. Avella.

INTRODUCTION

The history and theory of current-sensitive single-gun color CRTs have been well detailed by Sisneros et al. (Refs. 1, 2, 3). These investigators did extensive and pioneer work on the development of such tubes based on screens comprising mixtures of phosphors differing in their emission color and luminance versus current density behavior. This report describes the results of a program to extend the investigations in this area and to explore new concepts. Research has been conducted in accordance with the objectives set forth in the contract digest as follows:

- Investigate techniques for producing nonlinear current-brightness relationships in phosphors.

- Develop phosphor mixtures that exhibit hue change with change of beam current at substantially constant accelerating voltage, and where at least one of the phosphors has a nonlinear current-brightness relationship.
- Evaluate means for minimizing apparent brightness differences of the phosphor emissions as beam current is changed.
- Select color combinations providing useful applications and identify such applications.
- Identify means for producing useful brightness and/or contrast levels, particularly in the presence of reasonable amounts of ambient illumination.
- Fabricate and deliver to ERC at the completion of the fourth, seventh, and tenth months of effort a sample tube to demonstrate the accomplishments of the research. This tube may be of any convenient size, but should be electrically compatible with electrical characteristics and deflection angles to be agreed upon during performance.

These objectives may be restated in terms of three major experimental efforts:

- Synthesis and evaluation of spectral shift phosphors, i.e., phosphors that individually exhibit a current-induced shift of emission chromaticity.
- Synthesis of phosphors with nonlinear luminance-current density characteristics and evaluation of these phosphors in multi-phosphor screens.
- Selection of absorption filters to maximize contrast and color gamut while minimizing the luminance differential at the operating extremes of current density.

In the context of this program the fabrication of sample CRTs was intended to fall within the area of phosphor and/or filter evaluation; however, subsequent requests by the contract Technical Monitor for sample CRTs of specific types established tube fabrication as a fourth major effort.

TECHNICAL DISCUSSION

Phosphor Preparation

Unless otherwise specified phosphors were synthesized by the usual techniques of solid-state chemistry using luminescent grade materials or their equivalents. Compound formation was verified by x-ray diffractometry.

Cathodoluminescence Measurements

Measurements of luminance and chromaticity were made on phosphors settled on the conductive side of tin oxide coated 1x1-inch glass (or fused silica) slides positioned in a demountable CRT apparatus capable of holding ten such slides. A standard TV raster compressed to 1x2 inches at an accelerating potential of 10 kV provided current densities averaged over time of 0.05 to 10.0 $\mu A/cm^2$. However, measurements made below 0.10 and above 5.0 $\mu A/cm^2$ were not sufficiently precise to be reliable. Sealed CRTs were also driven with the electronics portion of the demountable CRT apparatus and, therefore, experienced similar operating conditions as the settled slides.

Luminance values were obtained with a Gamma Scientific Photometer Model No. 2020 calibrated to the luminosity function. In most cases the luminance values are reported relative to a commercial P-1 standard. For the sealed CRTs luminance values were obtained by comparison with a Spectra regulated brightness source (Photo Research Corp.) or a Gamma Scientific standard luminance source.

Chromaticity data were obtained with a Jarrell-Ash Tristimulus Spectroradiometer which incorporates an analog computer to provide CIE chromaticity coordinates (x, y) directly. Coordinates for the MacAdam "nearly" uniform chromaticity diagram (u, v) were calculated from the CIE chromaticity coordinates. The magnitude of chromaticity shifts were determined from distances between (u, v) points as given by $(\Delta u^2 + \Delta v^2)^{\frac{1}{2}}$. Emission spectra were recorded with the same instrument directly in terms of relative radiated energy vs. wavelength.

To compare the degree of nonlinear behavior of different phosphors, use is made of a linearity ratio as given by $(L_b/j_b)/(L_a/j_a)$, where L_n is the relative luminance measured at a current density j_n. It was found empirically that the nonlinear characteristic is most pronounced at current densities up to about 2 $\mu A/cm^2$; therefore, j_a and j_b were fixed at 0.1 and 2.0 $\mu A/cm^2$, respectively. A linearity ratio of 1 indicates linear behavior; a ratio less than 1 indicates the degree of sublinear behavior while a ratio greater than 1 quantifies the superlinear behavior.

Absorption Filters

Absorption filters may improve the operation of CRTs with current-induced color shifts in several ways:

- Expansion of color gamut by removing intermediate portions of the emission spectrum.
- Saturation or shifting of a phosphor emission by removing the undesirable emissions.
- Reduction of the differential between luminance values at high and low current densities by absorbing part of the emission arising at high current densities.
- Increase in contrast through the absorption of ambient light in spectral regions where the phosphors do not emit.

The last technique received least attention because of the difficulty in achieving the close physical match needed between the filter and the curved CRT faceplate to eliminate extraneous reflections. Most emphasis was placed on the first two approaches.

To fulfill the above functions, filters are needed having narrow absorption bands in the visible spectrum. Glasses containing trivalent lanthanide ions were found applicable in this respect as were a series of metal porphyrins. The most useful among these were Nd and Di (didymium) glasses and Cu-porphyrin. The transmission spectra of these filters are reproduced in Figures 1, 2, and 3, respectively. Since Di consists essentially of Nd and Pr, the Di filter transmission spectrum closely resembles that of Nd, but with additional absorption in the blue and orange regions. Vanadyl porphyrin also proved useful; its transmission spectrum resembles that of the Cu compound, but has its transmission minimum shifted from 540 to 548 nm. Sharp cut-off filters were considered for absorption of ambient light of wavelength shorter than that of the phosphor emission.

Experimentation with the filters will be discussed in the sections devoted to the phosphors with which they were evaluated.

Spectral Shift Phosphors

Meyer and Palilla (Ref. 4) have shown that the spectral peak of the cathodoluminescence from red-emitting (Cd, Zn)S:Ag phosphors shifts toward shorter wavelength with an increase in current density. These phosphors are referred to as spectral shift phosphors. Five different samples of these phosphors were examined for chromaticity shift and for the effect of Nd and Di filters thereon. The results are given in Table I. These measurements were made early in the program before procedures were

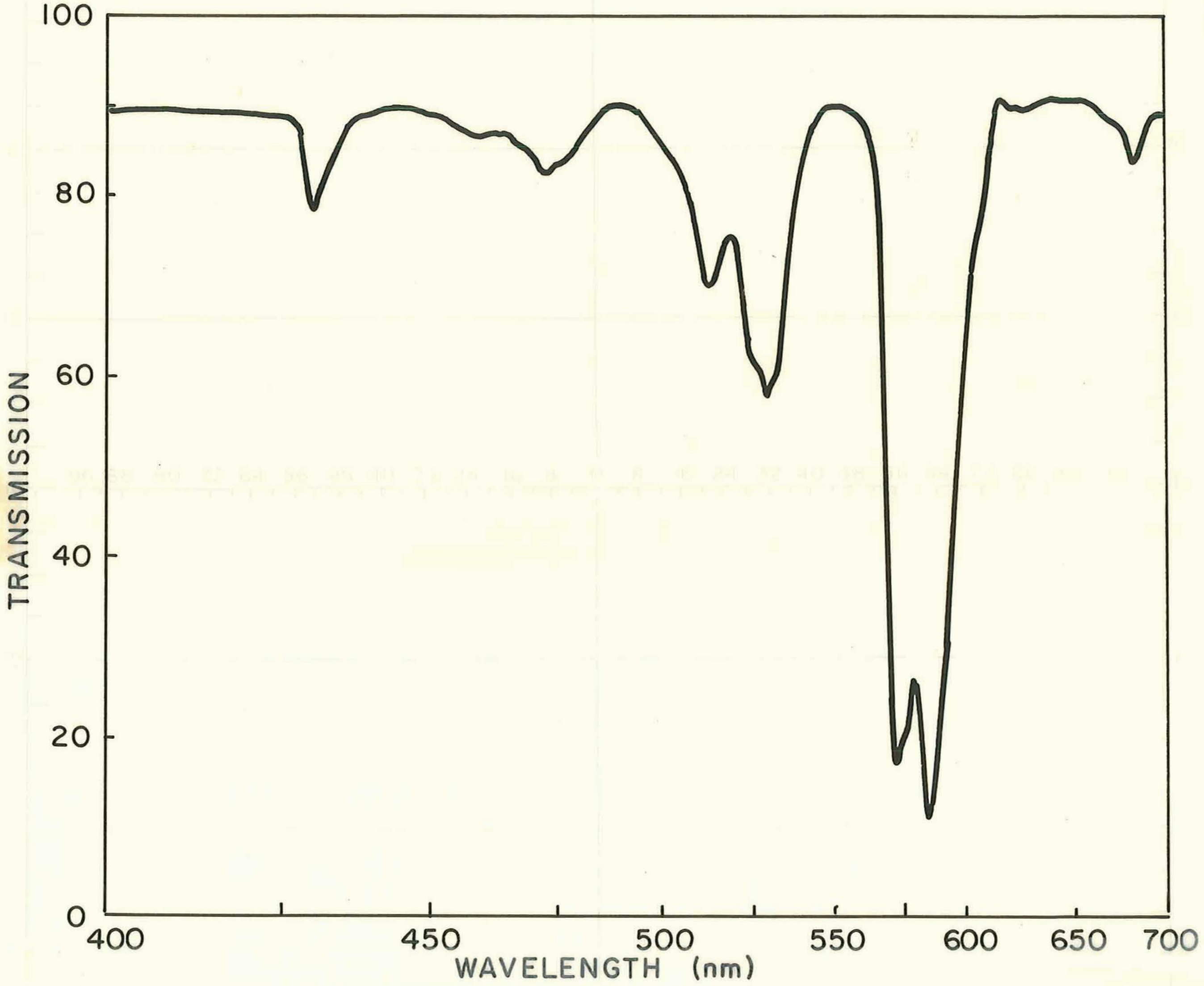

Fig. 1. Transmission spectrum of neodymium glass filter.

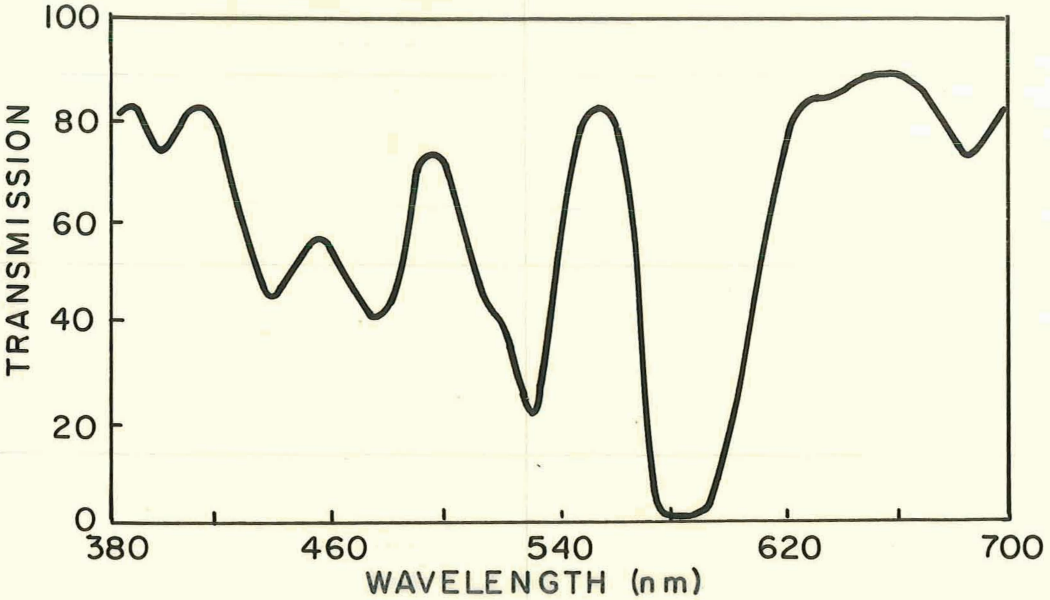

Fig. 2. Transmission spectrum of didymium glass filter.

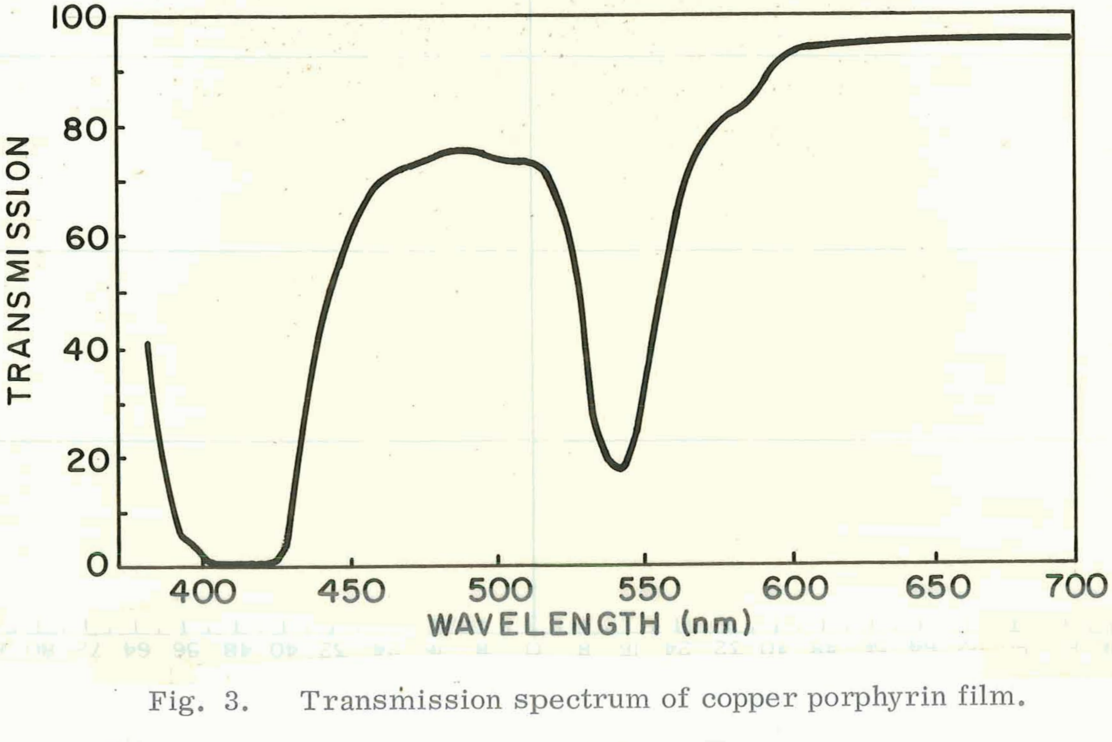

Fig. 3. Transmission spectrum of copper porphyrin film.

TABLE I

CHROMATICITY DATA FOR (Cd, Zn)S:Ag SPECTRAL PHOSPHORS MEASURED AT DIFFERENT CURRENT DENSITIES USING ABSORPTION FILTERS

Sample	Filter	0.5 $\mu A/cm^2$ (20 kV)		5 $\mu A/cm^2$ (20 kV)		Chromaticity Shift $(\Delta u^2 + \Delta v^2)^{\frac{1}{2}}$
		(x, y)	(u, v)	(x, y)	(u, v)	
RCA 33-Z-237A	None	.657, .346	.450, .356	.641, .361	.424, .358	.026
Sylvania RX-27	None	.652, .352	.441, .357	.644, .358	.429, .358	.012
Sylvania R-8	None	.650, .352	.439, .357	.641, .361	.424, .358	.015
Sylvania FS-15958	None	.643, .359	.427, .358	.634, .367	.413, .359	.014
Sylvania TTP-1875	None	.658, .344	.453, .355	.649, .354	.435, .357	.018
RCA 33-Z-237A	Neodymium	.676, .325	.496, .351	.659, .343	.455, .355	.041
Sylvania RX-27	Neodymium	.673, .330	.480, .353	.666, .336	.467, .354	.013
Sylvania R-8	Neodymium	.671, .332	.476, .353	.659, .344	.454, .355	.022
Sylvania FS-15958	Neodymium	.665, .337	.466, .354	.653, .348	.445, .356	.021
Sylvania TTP-1875	Neodymium	.678, .325	.489, .352	.679, .323	.492, .351	.003
RCA 33-Z-237A	Didymium	.684, .319	.501, .351	.681, .322	.495, .351	.006
Sylvania RX-27	Didymium	.678, .325	.504, .350	.674, .335	.489, .352	.015
Sylvania R-8	Didymium	.679, .324	.495, .351	.686, .318	.491, .352	.004
Sylvania FS-15958	Didymium	.676, .326	.486, .352	.674, .328	.482, .352	.004
Sylvania TTP-1875	Didymium	.682, .321	.497, .351	.682, .321	.497, .351	---

standardized; consequently, the accelerating voltage was 20 kV rather than 10 kV and the current densities differed only by a factor of ten instead of the more desirable factors of 50 or 100, so that the shifts in chromaticity were small, in some cases within experimental error. (See the section on Fabrication of Sample CRTs [page 10] for measurements at other current densities.) It can be seen that the phosphors do differ in the degree of spectral shift experienced at these current densities and in the effect on those shifts produced by the filters. The greatest intrinsic shift was produced by the RCA phosphor in which case it was further extended by the Nd filter but apparently was reduced by the Di filter. Figure 4 (a, b, and c) presents spectra of the unfiltered and filtered emission from the RCA phosphor operated at 0.5 $\mu A/cm^2$. Note that both filters shift the emissions toward deeper red and that the greater absorption of the Di filter in the orange-red is probably responsible for the diminished spectral shift at the higher current density.

One approach to designing a spectral shift phosphor is to activate a compound capable of host emission with an activator producing a different emission color. If the activator is present in low concentration, the activator centers may saturate at high current densities allowing the host emission to dominate. Several phosphors of this type were prepared and the results are summarized in Table II. $MgGa_2O_4$:Mn is the most successful of these phosphors producing a blue-green to green shift, while $CaGa_4O_7$:Mn is next, shifting from yellowish orange to bluish white. The chromaticity values for four of these phosphors are also plotted on a Kelly Chart in Figure 5. Reduction of activator concentrations below those given did not expand the chromaticity gamut, while higher concentrations reduced or eliminated the shift. It appears that a criterion for a significant spectral shift is efficient energy transfer from host to activator so that low-current-density excitation can produce activator emission at the low activator concentrations required for saturation to occur at high current densities. Thus, the gallate and silicate phosphors produce fair shifts and the tungstates do not. These spectral shift phosphors were also evaluated in conjunction with absorption filters, but no improvements were obtained. The method given above for designing spectral shift phosphors is effective; however, the color gamuts obtained have been small relative to those possible with multi-phosphor screens as will be discussed below.

Nonlinear Phosphors

Throughout the period of this contract there has been a program of examining available phosphors for nonlinear luminance-current density behavior. Many of these

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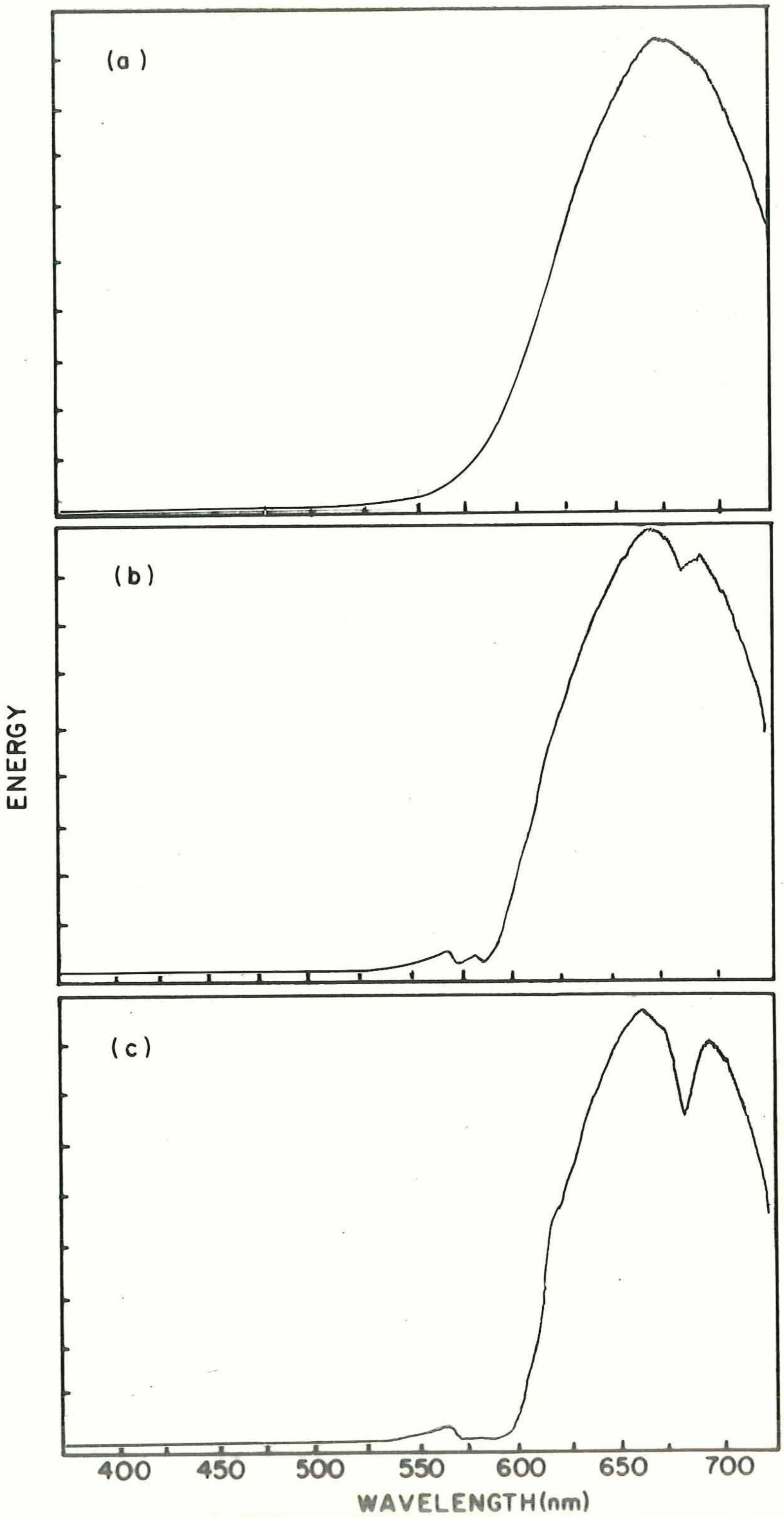

Fig. 4. Cathodoluminescence spectrum of (Cd, Zn)S:Ag phosphor (RCA 33-Z-237A): (a) no filter, (b) measured through Nd-glass filter, and (c) measured through Di-glass filter.

TABLE II

PHOSPHORS EVALUATED FOR CURRENT-SENSITIVE CHROMATICITY AT 10 kV

Sample No.	Host:Activator	Formulated Activator Concn. (a/o)	Luminance at 0.5 μA/cm^2 (P-1 set at 10)	Chromaticity Data								
				0.1 μA/cm^2				10.0 μA/cm^2				Chromaticity Shift $(\Delta u^2 + \Delta v^2)^{\frac{1}{2}}$
				x	y	u	v	x	y	u	v	
TES-69-6	$MgGa_2O_4$:Mn	0.02	0.4	.132	.429	.067	.326	.148	.318	.091	.293	.041
TES-69-15	$CaGa_4O_7$:Mn	0.015	0.51	.479	.462	.252	.365	.433	.434	.236	.354	.019
B1512-23A	$K_2O \cdot 6Ga_2O_3$:Mn	0.8	0.92	.098	.601	.039	.360	.128	.572	.053	.357	.014
B1512-27ABC, 23B	$K_2O \cdot 6(Ga, Al)_2O_3$:Mn	1.0	0.56	.127	.560	.054	.355	.147	.514	.078	.347	.025
B1512-28B	$MgGaAlO_4$:Mn	0.02	0.27	qualitatively similar to TES-69-6								
DP160-7*	Zn_2SiO_4:Mn	0.01	0.9	shift from yellowish green to bluish white								
B1356-86B	$CaWO_4$:Tb	0.2	low	shift from very slightly greenish blue to blue								
B1356-86G	$CaWO_4$:Eu	0.002	low	shift from very slightly reddish blue to blue								
B841-83A	Ca_3UO_6:Eu	3.0	very low	-				-				no shift
B841-83B	Sr_3UO_6:Eu	3.0	very low	-				-				no shift

*Courtesy of Sylvania Chemical and Metallurgical Division

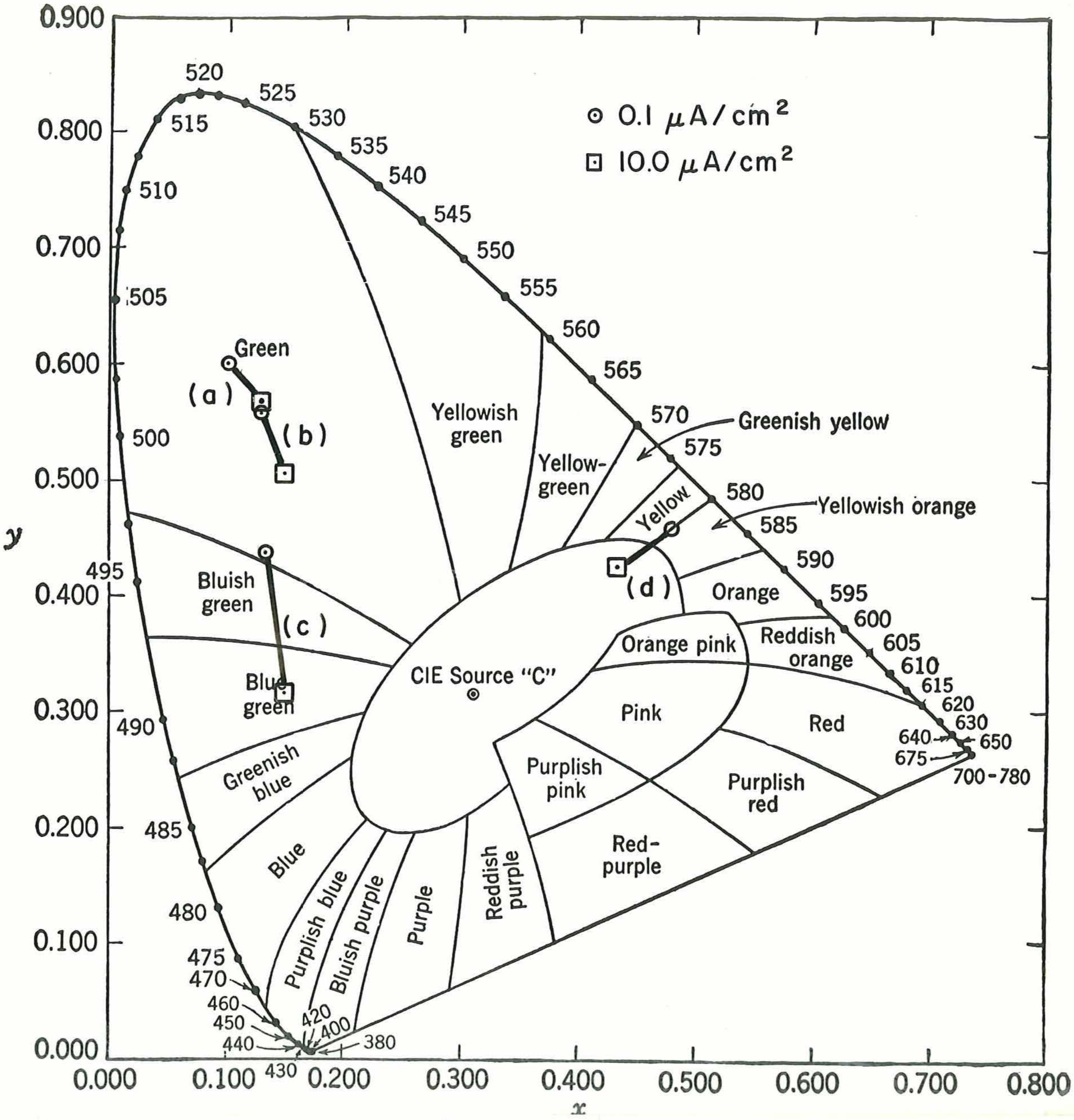

Fig. 5. Chromaticity shifts of phosphors excited at two current densities: (a) $K_2O \cdot 6Ga_2O_3$:Mn (0.8 a/o), (b) $K_2O \cdot 6\ (Ga, Al)_2O_3$:Mn (1 a/o), (c) $MgGa_2O_4$:Mn (0.015 a/o), (d) $CaGa_4O_7$:Mn (0.02 a/o).

phosphors are proprietary and are therefore not listed in this report; however, none of the proprietary phosphors were found to be nonlinear. Furthermore, among the nonlinear (non-proprietary) phosphors turned up by the survey not one was superlinear. The research on superlinear and sublinear phosphors will be reviewed separately.

Superlinear Phosphors.--The discovery by Sisneros et al. (Ref. 1) that certain (Zn, Cd)S:Ag, Ni phosphors exhibit a superlinear luminance-current density relationship under electron beam excitation made possible the development of a current-sensitive single-gun color CRT having a substantially wider color gamut than was previously attained using mixtures of linear with sublinear phosphors. However, many problems still remained with the superlinear sulfides, not the least of which was synthesis reproducibility. Considerable time was expended in developing the most effective synthesis procedures. These are outlined below for two optimized formulations (concentrations in weight percent):

Reddish Orange-Emitting $70CdS \cdot 30ZnS:5 \cdot 10^{-3}Ag, 5 \cdot 10^{-4}Ni$--

- Slurry 30g ZnS, 70g CdS, 0.0013g $NiSO_4$ and 2.0g NaCl flux.
- Fire at 750°C for 2 hours.
- Discard top layer and slurry remainder with 0.008g $AgNO_3$.
- Fire at 750°C for 2 hours.
- Discard top layer; wash remainder with cold water and dry at 100°C.

Green-Emitting $55ZnS \cdot 45CdS:5 \cdot 10^{-3}Ag, 7.5 \cdot 10^{-4}Ni$--

- Slurry 55g ZnS, 45g CdS, 0.0020g $NiSo_4$, 0.008g $AgNO_3$ and 2g NaCl flux.
- Fire at 850°C for 2 hours.
- Discard top layer; wash remainder with cold water and dry at 100°C.

Lowering the firing temperature to 750°C for the high CdS phosphor greatly reduced CdS volatilization and, therefore, improved reproducibility. Nonetheless, in this phosphor system 100 percent reproducibility remained elusive. Table III presents cathodoluminescence date for four typical superlinear sulfides having small variation in Ni concentrations.

The previous contractors (Refs. 1, 2) had found that a reduction in the CdS concentration below 40 w/o or an increase above 70 w/o nullified the superlinear effect.

TABLE III

CATHODOLUMINESCENCE OF SUPERLINEAR (Zn, Cd)S: Ag, Ni PHOSPHORS

Sample No.	ZnS/CdS Weight Ratio	Ni Concn. (w/o)	Emission Color	Relative Luminance at 0.5 $\mu A/cm^2$, 10 kV (P-1 set at 10.0)	Linearity Ratio*
FP-4306	30/70	$5 \cdot 10^{-4}$	red-orange	0.75	4.5
FP-4308	30/70	$7.5 \cdot 10^{-4}$	red-orange	0.70	5.0
FP-4310	55/45	$7.5 \cdot 10^{-4}$	green	0.80	6.3
FP-4311	55/45	$6.0 \cdot 10^{-4}$	green	1.65	3.5

*$(L_b/j_b)/(L_a/j_a)$ where L_n is the relative luminance measured at a current density j_n with j_a and j_b fixed at 0.1 and 2.0 $\mu A/cm^2$, respectively.

Since it would be advantageous to have a redder superlinear phosphor than that prepared with 70 w/o, syntheses were performed with small incremental increases of CdS between 70 and 80 w/o. The results are summarized in Table IV (samples FP-4355 through 4359). Note that the CdS concentrations found by chemical analysis were only slightly lower than the formulated values. The effect of increasing CdS was progressive depression of the linearity ratio. Visual comparison of the sample emissions did not indicate any substantial effect on the chromaticities by the increased CdS concentration. Working at the other end of the spectrum, the lower limit of useful CdS concentration was found to be approximately 43 w/o, beyond which the linearity ratio was again reduced and the emission color began to desaturate. These results verified those previously reported (Refs. 1, 2).

Another series of experiments was performed to determine the effect of small substitutions of ZnSe for ZnS in a superlinear sulfide. For this purpose a formulation yielding green emission was chosen, and ZnSe concentrations of 1, 2, and 5 w/o were used. The cathodoluminescence results are given in Table IV for samples FP-4344 through FP4347. ZnSe substitutions greater than 1 w/o had a deleterious effect on both luminance and linearity ratio.

Excitation with cascade phosphors.--The superlinear variation of phosphor luminance with intensity of exciting radiation was known for photoluminescence before cathodoluminescence (Ref. 5), and it was thought that the effect was more pronounced with ultraviolet excitation. This led to experiments to determine whether the superlinear behavior of a phosphor could be enhanced by introducing a cascade phosphor into the CRT screen. Three UV-emitting phosphors were chosen for the initial experiments: $BaSi_2O_5$:Pb (Sylvania No. 2011), $Ca_3(PO_4)_2$:Tl (NBS 1033) and YOCl:Ce.

UV-transmitting fused silica slides were coated with these phosphors and positioned in the demountable CRT. Glass slides were coated with superlinear red- and green-emitting (Zn, Cd)S:Ag, Ni phosphors and also a blue-emitting ZnS:Ag, Co, and these slides were placed in the demountable CRT with their phosphors against the uncoated viewing sides of the fused silica slides. In this way cathodo-excited uv emission could pass through the fused silica and excite the sulfide phosphors without interference from cathodo-excited emission of the sulfide phosphors. The superlinear phosphors proved to have such poor response to uv excitation that the output of the cascade phosphors was not intense enough to produce luminescence, and measurements

TABLE IV

CATHODOLUMINESCENCE OF MODIFIED SUPERLINEAR PHOSPHORS

$(55-x)\,ZnS \cdot xZnSe \cdot 45CdS{:}5 \cdot 10^{-3}\,Ag,\ 7.5 \cdot 10^{-4}\,Ni^{*}$

$(100-y)\,ZnS \cdot yCdS{:}5 \cdot 10^{-4}\,Ni^{*}$

Sample No.	xZnSe (w/o)	y CdS formulation (w/o)	y CdS analysis (w/o)	Relative Luminance at 0.5 μA/cm^2, 10 kV (P-1 set at 10.0)	Linearity Ratio**
FP-4344	0	-	-	0.80	6.7
FP-4345	1	-	-	0.88	6.2
FP-4346	2	-	-	0.21	2.2
FP-4347	5	-	-	0.15	1.2
FP-4355	-	70	68	0.49	4.6
FP-4356	-	72	not analyzed	0.51	4.2
FP-4357	-	74	72	0.38	3.2
FP-4358	-	76	not analyzed	0.42	2.9
FP-4359	-	80	77	0.51	2.0

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*Concentrations in weight percent

**$(L_b/j_b)/(L_a/j_a)$ where L_n is the relative luminance measured at a current density j_n with j_a and j_b fixed at 0.1 and 2.0 μA/cm^2, respectively.

could not be made. This was also true of the ZnS:Ag, Co phosphor. No further experimentation of this type was performed.

Sublinear phosphors.--It is fairly safe to state that all cathodoluminescent phosphors exhibit sublinear response of their emission intensity when excited by an electron beam of sufficiently high current density, i.e., their emissions saturate. However, the current densities required to produce saturation vary from phosphor to phosphor. For the purposes of this program saturation should occur by about 2 $\mu A/cm^2$ in order for the phosphor to be useful. The best known sublinear phosphors are those based on (Zn, Cd)S:Ag, and they were used successfully by Sisneros et al. (Refs. 1, 2) in preparing current-sensitive screens. However, Sisneros et al. developed more useful sublinear phosphors by using the technique discussed in the section on Spectral Shift Phosphors. They lowered the activator concentration to a level where the activator centers would become saturated at high current densities. Unlike the spectral shift phosphors, however, the activator concentration was adjusted to supress the host emission, or hosts incapable of host emission were used. In this way they obtained good sublinear response from green-emitting Zn_2SiO_4:Mn and red-emitting $(Zn, Cd)_3(PO_4)_2$:Mn.

The above approach was utilized in surveying for and attempting synthesis of sublinear phosphors, i.e., activator concentrations were generally kept low. Sufficient sublinear Zn_2SiO_4:Mn and $(Zn, Cd)_3(PO_4)_2$:Mn were synthesized for evaluation with filters and comparison with other phosphors but no further research was undertaken on these particular phosphors. Many phosphors were tested and their emissions were found to be approximately linear, slightly sublinear and/or very weak. These phosphors are listed in Table V along with their cathodoluminescence data. Other phosphors were more interesting in that they were moderately sublinear and yielded substantial luminance. These include the $MgGa_2O_4$:Mn and $CaGa_4O_7$:Mn systems discussed above with the spectral shift phosphors and also $MgAl_2O_4$:Mn and $MgGaAlO_4$:Mn. The effect of Mn concentration on the sublinearity of these phosphors was evaluated and the results are given in Table VI. In general, the lowest Mn concentrations yield fair to good sublinearity, but at these activator levels, chromaticity shifts occur. Higher Mn levels eliminate the shifts but raise the linearity ratios. As a result, no further development of these phosphors was undertaken in this phase of the program.

Finally, the survey produced two green-emitting phosphors which displayed good sublinearity and usable luminance values: $K_2O \cdot (5\text{-}6)Ga_2O_3$:Mn and $NaTaO_3$:Tb. The

TABLE V

CATHODOLUMINESCENCE OF PHOSPHORS AT DIFFERENT CURRENT DENSITIES

Sample No.	Formulation	Activator Concentration (a/o)	Emission Color	Relative Luminance at 0.5 $\mu A/cm^2$, 10 kV	Linearity Ratio*
P-1 Standard	Zn_2SiO_4:Mn	-	yellowish-green	10	0.90
FP4372	$Y_3Ga_5O_8$:Eu	0.15	red	0.56	0.84
FP3539	"	15	"	4.0	0.90
B572-91D	$NaTaO_3$:Eu	2	"	0.10	1.1
E	"	5	"	0.09	1.1
B1512-35B	"	1	"	0.08	1
RKB891	$LiAl_5O_8$:Fe	1	"	extremely weak	approx. linear
B1512-38A	$LiAl_5O_8$:Mn	0.5	green	0.19	0.55
B1512-42	"	2.0	"	0.63	0.72
TES-69-4	$MgGa_2O_4$	none	blue-white	0.55	0.8
TES-69-8	$CaGa_4O_7$	"	"	0.22	0.8
B642-23C	$YTaO_4$:Tb	1.0	green	4.9	0.93
E	"	5.0	"	5.9	1.0
B535-37A	$Ca_3(BO_3)_2$:Tb	0.5	"	2.0	1.0
C	"	1.5	"	2.0	1.1
E	"	3.0	"	3.3	1.0
B572-10A	$InBO_3$:Tb	0.1	"	2.5	1.1
B	"	0.5	"	9.0	1.1
C	"	1.0	"	11.8	1.1

*$(L_b/j_b)/(L_a/j_a)$ where L_n is the relative luminance measured at current density j_n with j_a and j_b fixed at 0.1 and 2.0 $\mu A/cm^2$, respectively.

TABLE VI

THE EFFECT OF ACTIVATOR CONCENTRATION ON THE SUBLINEARITY OF SEVERAL PHOSPHORS

Sample No.	Formulation	Activator Concentration	Emission Color	Relative Luminance at 0.5 μA/cm^2, 10 kV (P-1 set at 10)	Linearity Ratio*
B1512-28A	$MgGa_2O_4$:Mn	0.06 a/o	shifts bluish-green to greenish-blue	1.2	0.70
B	$MgGaAlO_4$:Mn	0.021	shifts bluish-green to blue	0.27	0.43
C	"	0.063	slightly yellowish green	0.60	0.70
D	"	0.10	"	0.95	0.70
E	"	0.50	"	1.40	1.07
F	$MgAl_2O_4$:Mn	0.06	yellowish green	0.81	0.70
G	"	0.10	"	1.20	0.83
H	"	0.5	"	1.25	1.04
B1512-21C	$MgGa_2O_4$:Mn	0.06	green	0.97	0.71
D	"	0.02	shifts bluish green to blue	0.66	0.43
TES-69-9	$CaGa_4O_7$:Mn	50 ppm	yellow	1.35	0.64
TES-69-15	"	20 ppm	shifts yellow orange to bluish white	0.51	0.54

*$(L_b/j_b)/(L_a/j_a)$ where L_n is the relative luminance at current density j_n, with j_a and j_b fixed at 0.1 and 2.0 μA/cm^2, respectively.

results obtained from these phosphors were unexpected in view of their high activator concentrations. Furthermore, $NaTaO_3$:Tb is the first lanthanide-activated oxidic phosphor found to be truly sublinear, and it is especially interesting that this should be so considering that $NaTaO_3$:Eu proved to be linear (see Table V).

Table VII lists values of relative luminance and linearity ratio obtained for series of $K_2O \cdot 6Ga_2O_3$:Mn and $K_2O \cdot 5Ga_2O_3$:Mn as a function of activator concentration. The former were synthesized with KF and MnF_2 while the latter were prepared by the method of Hoffman and Brown (Ref. 6) using K_2CO_3 and $MnCO_3$. Although less effective under uv-excitation, the formulations with 6 Ga_2O_3 are better performers under cathode ray excitation in terms of brightness and sublinearity. Optimum results were obtained with approximately 1 a/o Mn, i.e., linearity ratios of 0.3 to 0.4 and luminance values 9 to 14 percent that of P-1 at 0.5 $\mu A/cm^2$. At the activator concentrations which yield good sublinearity, this phosphor can experience a small current-induced chromaticity shift as indicated in Table II and Figure 5. Attempts were made to eliminate the shift by altering the synthesis procedure. Emphasis was put on the means of incorporating the activator since the concentration for optimum sublinearity appeared to be a borderline case with respect to the ability to quench the host emission. Partial success was obtained in that samples with stable chromaticity and good sublinearity were prepared, but the problem of reproducibility still remained.

Compositional modifications of the potassium gallate phosphor were also evaluated. Partial and total substitution of Al for Ga and of Na for K were made; cathodoluminescence results are summarized in Table VIII. The effect of an increasing Al concentration was to make the emission slightly more yellow and to increase the linearity ratio up to the $K_2O \cdot 6Al_2O_3$:Mn end-member which has yellowish green linear emission. Chromaticity coordinates were obtained for a sample from another series which had a small aluminum concentration. These data, given in Table II and plotted in Figure 5, show slight desaturation rather than yellowish emission. The series formulated with increasing Na substitutions shows a nearly constant linearity ratio, a greener and a more intense emission up to the $Na_2O \cdot 6Ga_2O_3$:Mn which is substantially less sublinear than the K-gallate control. However, the low luminance value for the control sample indicates that synthesis of this series may have been less than optimum and implies that these results are questionable.

In the course of measurements on the aluminogallates with the demountable CRT, it was noted that luminance values dropped with increasing duration of exposure to the

TABLE VII

CATHODOLUMINESCENCE DATA FOR $K_2O \cdot nGa_2O_3:xMn$ PHOSPHORS

Sample No.	n	x	Relative Luminance at 10 kV 0.5 $\mu A/cm^2$	Linearity Ratio*
P-1	-	-	10.0	0.95
B1512-18A	6	0	0.11	0.5
B	6	0.001	0.32	0.28
C	6	0.01	0.97	0.31
D	6	0.10	2.8	0.55
E	6	0.15	3.0	0.60
F	6	0.20	2.7	0.70
G	5	0	0.17	0.5
H	5	0.001	0.32	0.4
I	5	0.01	0.35	0.5
J	5	0.10	0.27	0.4
K	5	0.15	2.0	0.75
L	5	0.20	2.0	0.85
B1512-23A	6	0.008	0.92	0.40
B	6	0.010	1.4	0.41
C	6	0.030	2.5	0.65
D	6	0.050	2.4	0.90
E	6	0.070	2.6	0.90
F	6	0.10	2.3	1.0

*$(L_b/j_b)/L_a/j_a)$ where L_n is the relative luminance at current density j_n, with j_a and j_b fixed at 0.1 and 2.0 $\mu A/cm^2$, respectively.

TABLE VIII

LUMINANCE vs CURRENT DENSITY FOR TANTALATE AND MODIFIED GALLATE PHOSPHORS

Sample No.	Formulation	Activator Concentration	Emission Color	Relative Luminance at 0.5 μA/cm^2, 10 kV	Linearity* Ratio
P-1	Zn_2SiO_4:Mn	-	yellow green	10.0	0.93
B1512-27A	$K_2O \cdot 6Ga_2O_3$:Mn	1.0 a/o	green	0.8	0.30
B	$K_2O \cdot 5.7Ga_2O_3 \cdot 0.3Al_2O_3$:Mn	"	increasingly yellowish	0.94	0.28
C	$K_2O \cdot 5.4Ga_2O_3 \cdot 0.6Al_2O_3$:Mn	"		1.05	0.34
D	$K_2O \cdot 4.8Ga_2O_3 \cdot 1.2Al_2O_3$:Mn	"		1.25	0.53
E	$K_2O \cdot 3.0Ga_2O_3 \cdot 3.0Al_2O_3$:Mn	"		0.68	0.45
F	$K_2O \cdot 6Al_2O_3$:Mn	"	yellowish green	1.00	1.09
B1512-26A	$K_2O \cdot 6Ga_2O_3$:Mn	"	bluish green	0.36	0.40
B	$K_{1.9}Na_{0.1}O \cdot 6Ga_2O_3$:Mn	"	"	0.42	0.34
C	$K_{1.8}Na_{0.2}O \cdot 6Ga_2O_3$:Mn	"	less blue	0.59	0.31
D	$K_{1.5}Na_{0.5}O \cdot 6Ga_2O_3$:Mn	"	"	0.69	0.38
E	$KNaO \cdot 6Ga_2O_3$:Mn	"	"	0.71	0.43
F	$Na_2O \cdot 6Ga_2O_3$:Mn	"	"	0.46	0.74
B1691-41A	$NaTaO_3$:Tb	2.0 a/o	yellow-green	0.60	0.35
B	"	"	"	2.0	0.22
C	"	"		2.2	0.24
D	"	"	"	2.15	0.22
E	"	3.0	"	2.3	0.22
F	"	1.0	"	2.1	0.23
G	"	0.5	"	2.45	0.21
B1691-15BCHI	"	2.0	"	1.86	0.22
B572-91B	"	2.0	"	1.0	0.18
C	"	5.0	"	0.20	0.27

*$(L_b/j_b)/(L_a/j_a)$ where L_n is the relative luminance at a current density j_n, with j_a and j_b fixed at 0.1 and 2.0 μA/cm^2.

electron beam. Since this result had not been observed previously, several old gallate samples were closely re-examined and found to act similarly. In some cases luminance losses up to 20 percent occurred in the first 10 minutes and levelled off at 30 percent after one hour of irradiation. The effect occurred at both low and high current densities and could not be correlated with variations in composition or synthesis parameters. The possibility of instrument malfunction was eliminated when steady luminance readings were obtained for other phosphors. However, measurements made on an aluminized gallate screen in a sealed 5-inch CRT failed to show time-dependent losses. The implication is that these losses result from a charging up of the un-aluminized phosphor screens used in the demountable CRT; and the charging, in turn, implies an unusually low sticking potential for the gallate phosphor. Therefore, it appears that quantitative comparisons of the cathodoluminescence properties of gallate samples may be possible only with aluminized screens. Re-measurements of some sublinear Zn_2SiO_4:Mn samples revealed a related behavior, but it differed in that after a preliminary drop luminance values climbed above the initial readings. No explanation has been found for this phenomenon.

$NaTaO_3$:Tb proved to be the most tractable of the phosphors investigated during this program. Synthesis reproducibility was good as evidenced by the cathodoluminescence data given in Table VIII for samples No. B1691-41 B, C, and D, all of which were prepared under the same conditions. (Different synthesis procedures were used for samples No. B1691-41A and B1691-15 BCHI.) The phosphor tolerated a Tb concentration range of 0.5 to 3 a/o with no significant variations in luminance values or linearity ratios. The linearity ratios are even lower than those reported for the most sublinear non-shifting Zn_2SiO_4:Mn samples (Refs. 1, 2), while luminance values are approximately the same. Chromaticity measurements on $NaTaO_3$:Tb (2 a/o) yielded CIE coordinates of $x = 0.347$, $y = 0.576$ ($u = 0.151$, $v = 0.375$), and essentially no current-induced chromaticity shift was observed. Finally, luminance values were found not to vary with duration of excitation. Another advantage of this phosphor became evident in the tube fabrication phase of the program and will be discussed in the next section.

Fabrication of Sample CRTs

Many phosphor-filter combinations were examined in the demountable CRT — first visually then instrumentally — in order to choose the best combination for fabrication into sample CRTs. However, chromaticity data are given in Table IX only for the CRTs

TABLE IX

CATHODOLUMINESCENCE OF SAMPLE CRTs OPERATED AT 10 kV

CRT No.	Phosphors	Superlinear / Sublinear Weight Ratio	Filter	Current Density ($\mu A/cm^2$)	Luminance ((ft-L)	Chromaticity Values				
						x	y	u	v	Color Gamut $(\Delta u^2 + \Delta v^2)^{\frac{1}{2}}$
B1691-34B	(Cd, Zn)S:Ag	-	none	0.1	2.2	.677	.336	.477	.355	-
	RCA 33-Z-237A		"	10.0	135.0	.640	.368	.417	.360	.060
B1691-34B	(Cd, Zn)S:Ag	-	Nd-glass*	0.1	1.7	.702	.316	.521	.351	-
	RCA 33-Z-237A		"	10.0	100.0	.662	.348	.453	.357	.068
B1691-30Cu	(Cd, Zn)S:Ag, Ni	3.5/1	Cu-porphyrin**	0.1	0.41	.287	.650	.112	.381	-
	Zn_2SiO_4:Mn			10.0	24.5	.331	.625	.135	.381	.023
B1691-73B	(Cd, Zn)S:Ag, Ni	3/1	none	0.1	0.53	.293	.565	.127	.369	-
			"	1.0	3.20	.420	.495	.207	.367	.080
	$K_2O \cdot 6Ga_2O_3$:Mn		"	5.0	18.7	.496	.442	.271	.363	.144
B1850-4A	(Cd, Zn)S:Ag, Ni	2/1	none	0.1	1.9	.421	.546	.193	.377	-
			"	1.0	8.1	.520	.464	.276	.369	.083
	$NaTaO_3$:Tb		"	5.0	34.0	.557	.435	.314	.367	.121
B1850-4A	(Cd, Zn)S:Ag, Ni	2/1	Nd-glass *	0.1	1.4	.402	.559	.181	.376	-
			"	1.0	5.7	.509	.470	.268	.370	.087
	$NaTaO_3$:Tb		"	5.0	23.0	.559	.429	.318	.365	.138

* 38% transmission at 585 nm.
** 50% transmission at 540 nm.

which do represent optimized results except for CRT No. B1691-30 Cu where reference must be made to measurements using the demountable CRT.

First delivery.--For the first delivery the contracting agency requested two CRTs with different screens and both differing in tube type from the originally intended 5-inch round Sylvania SC5780 in being the 9-inch rectangular Sylvania type ST4716A. Many fabrication problems were encountered with these tubes, mostly resulting from the small neck size. Furthermore, brightness losses were inevitable because of the 52 percent transmittance neutral density filter included in the faceplate. CRT No. B1691-34B was prepared with the RCA spectral-shift (Cd, Zn)S:Ag phosphor discussed in the section on Spectral Shift Phosphors. The test data in Table IX demonstrate the expanded color gamut available when the previously used current-density range of 0.5 to 5.0 $\mu A/cm^2$ (Table I) was expanded to 0.1 to 10.0 $\mu A/cm^2$. A further expansion in the color gamut of 13 percent was realized by the separate Nd-glass filter of faceplate size included in the delivery.

CRT No. B1691-30Cu was screened with a phosphor mixture comprising superlinear red-orange emitting (Cd, Zn)S:Ag, Ni and a still unoptimized sublinear Zn_2SiO_4:Mn in a 3.5/1 ratio by weight. For a current density range of 0.1 to 10.0 $\mu A/cm^2$, one-inch test screens in the demountable CRT had yielded a MacAdam chromaticity gamut of 0.092 which expanded to 0.099 using a Cu-porphyrin filter. The spectra from the demountable CRT are depicted in Figs. 6 and 7 and demonstrate the effect of the Cu-porphyrin filter in absorbing some of the yellow-green emission, thereby shifting the Zn_2SiO_4:Mn emission peak from about 528 to about 519 nm. In Table IX it will be noted that CRT No. B1591-30Cu produced a chromaticity gamut of only 0.023, and from examination of the screen during operation it was obvious that the output of the superlinear red-emitting phosphor was much lower at high current densities than had been observed in the demountable CRT.

A series of experiments utilizing 5-inch round CRTs were performed to isolate the fabrication parameter leading to degradation of the superlinear phosphor. It was found that the bake-out after aluminizing was the source of trouble. In the usual laboratory fabrication procedure the aluminized bulb is heated to 400°C in one hour, held at 400°C for about one hour and then allowed to cool for about 16 hours. When the bake out temperature was changed to 325°C with the heating, baking and cooling periods held to 1/2 hour each, good superlinear performance was obtained. It was determined

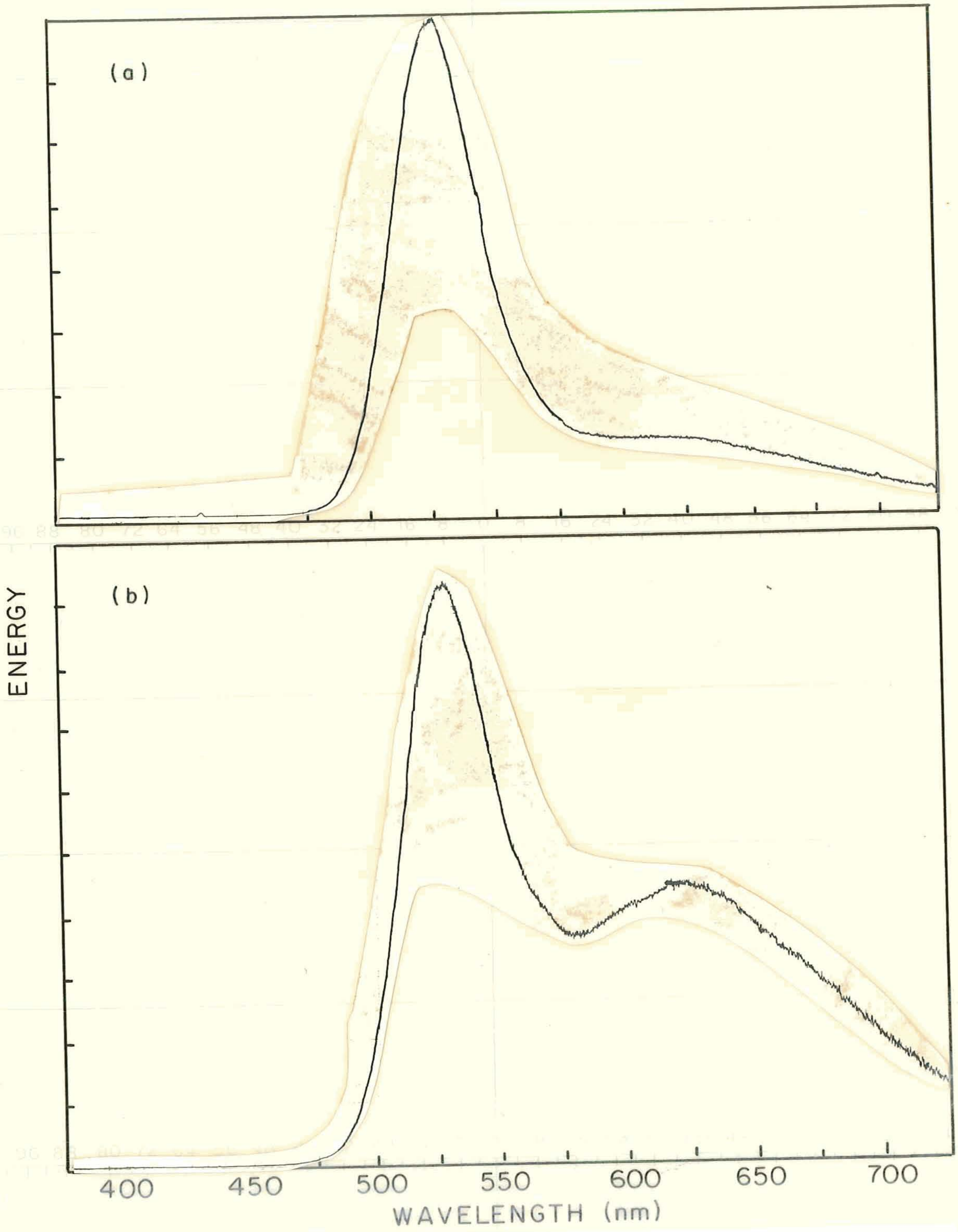

Fig. 6. Cathodoluminescence spectrum from screen comprising superlinear (Cd, Zn)S:Ag, Ni and sublinear Zn_2SiO_4:Mn operated at: (a) 0.1 μA/cm^2 and 10 kV, and (b) 10 μA/cm^2 and 10 kV.

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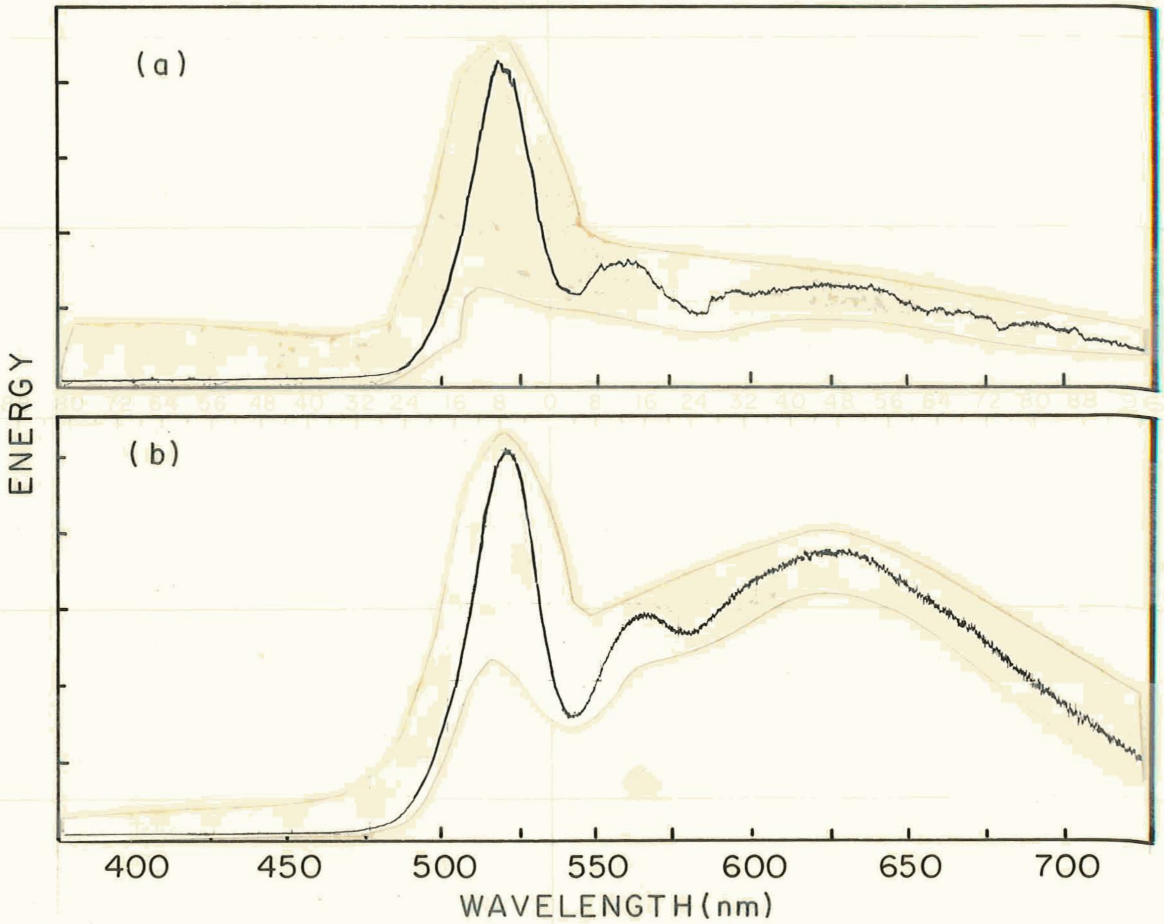

Fig. 7. Cathodoluminescence spectrum through Cu-porphyrin filter from screen comprising superlinear (Cd, Zn)S:Ag, Ni and sublinear Zn_2SiO_4:Mn operated at: (a) 0.1 $\mu A/cm^2$ and 10 kV, and (b) 10 $\mu A/cm^2$ and 10 kV.

that the extended bake-out at 400°C lowered the emission luminance at the higher current densities thereby reducing the linearity ratio by 50 percent.

Second delivery.--For the second delivery two 6-inch rectangular CRTs of Westinghouse type WX-30844 were requested having the same screen. A problem was encountered here in that Westinghouse was unwilling to release the required electron guns for our usage; therefore, the bulbs had to be screened here, then sent to Westinghouse for gun insertion and mounting.

The screen chosen for these tubes was a mixture of superlinear red-orange emitting (Cd, Zn)S:Ag, Ni and sublinear green-emitting $K_2O \cdot 6Ga_2O_3$:Mn. Westinghouse advised that their exhaust cycle utilized a 400°C bake-out for about 1/2 hour. In order to determine whether this exposure to 400°C would be deleterious to the temperature-sensitive superlinear phosphor, a 5-inch round CRT was fabricated here with a screen composed only of the superlinear phosphor. The bulb was baked at 325°C after being aluminized and then was baked at 400°C for 1/2 hour during the exhaust cycle. Comparison with another CRT containing the same phosphor but exhausted at 300°C showed that the higher exhaust temperature lowered the brightness at high current densities and, therefore, reduced the linearity ratio from 3.6 to 2.7. It was felt that CRTs yielding good color shifts would still be possible using this superlinear phosphor despite the possibility of some degradation. Accordingly, three WX-30844 bulbs were screened with a mixture of superlinear red sulfide and sublinear potassium gallate phosphors in a 3 to 1 weight ratio. In an attempt to compensate for possible degradation of the superlinear phosphor during exhaust, three bulbs were also screened with a 4 to 1 weight ratio of the same phosphors.

Evaluation of the completed WX-30844 CRTs revealed one which arced and five with non-uniform screens which had unusually weak emission from the gallate phosphor and, consequently, yielded no color shift. In view of these results, three 5-inch round SC-5780 CRTs were fabricated with a 3 to 1 mixture of the same phosphors under approximately optimum conditions. Two were delivered (B1691-73A and B1691-73C) and one (B1691-73B) was retained for testing; the data are listed in Table IX and the x, y coordinates are plotted in Figure 8. Note that for this and the next tube the highest reliable current density setting was reduced from 10 to 5 $\mu A/cm^2$ as some of the instrumental problems became better understood. The emission spectra at low and high current densities are given in Figures 9(a) and (b), respectively. For a green-to-red shift with increasing current density the color gamut obtained was second only to

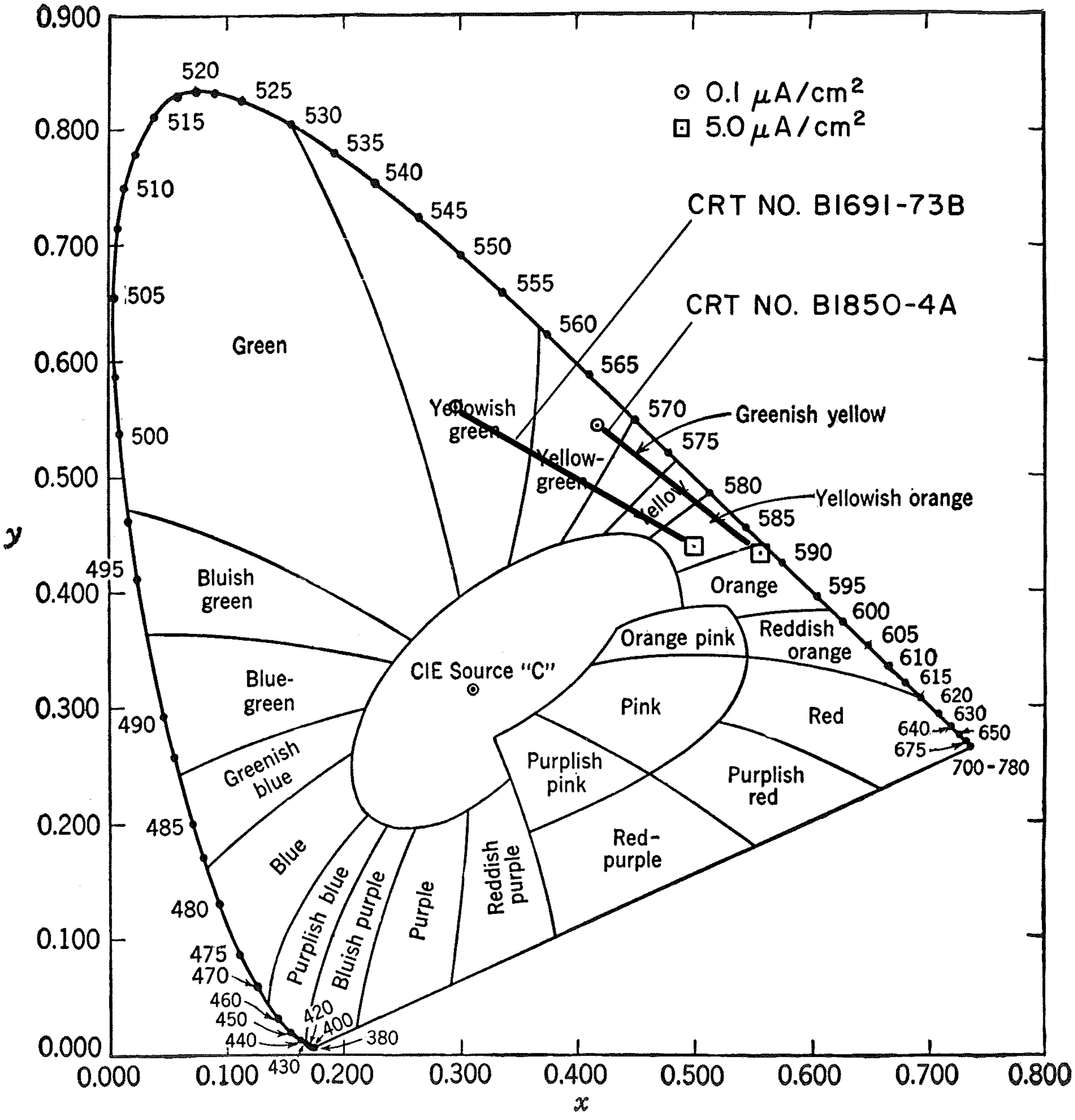

Fig. 8. Color gamuts produced by sample CRTs operated at 10 kV.

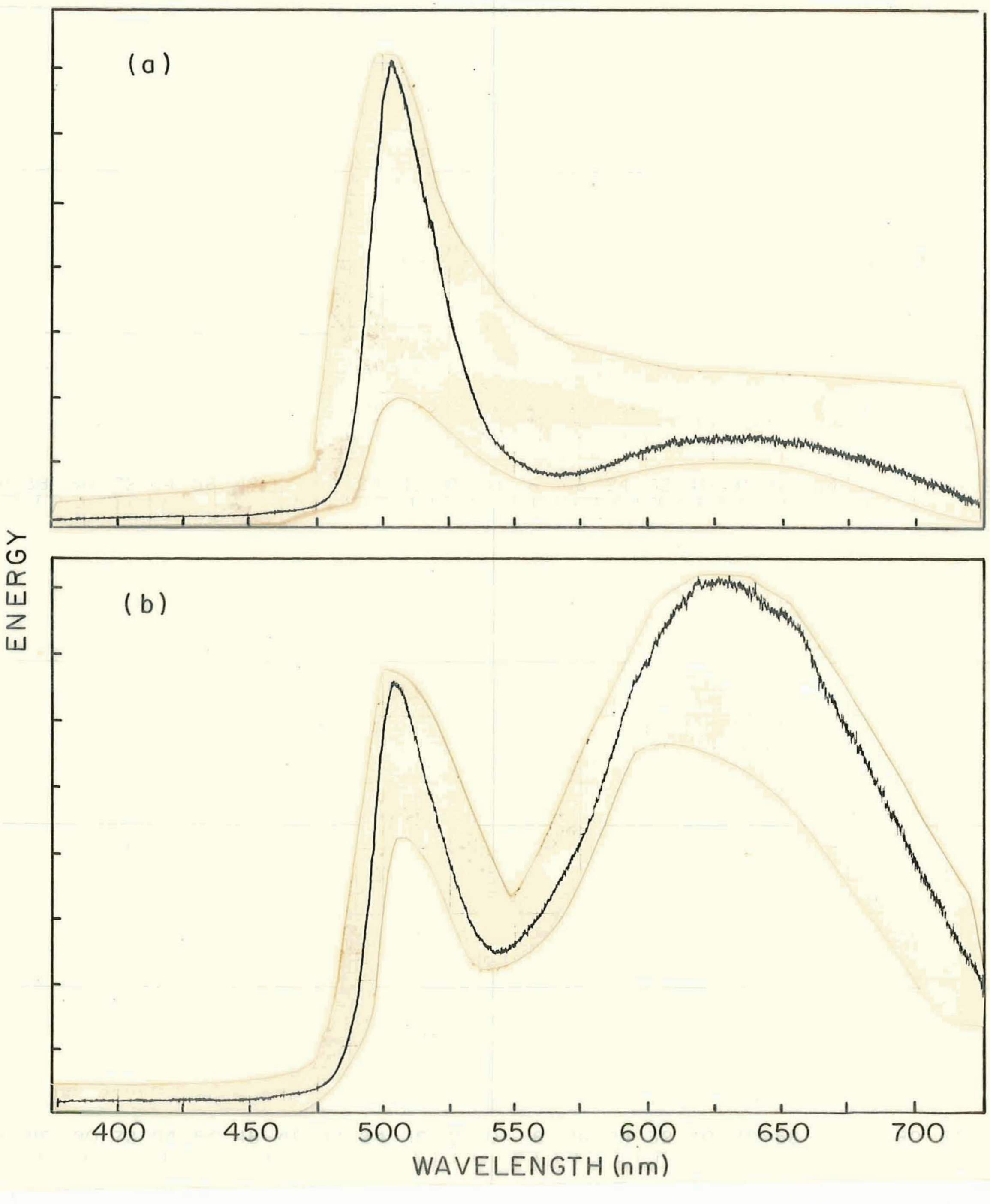

Fig. 9. Cathodoluminescence spectrum of CRT No. B1691-73B operated at: (a) 0.1 $\mu A/cm^2$ and 10 kV, and (b) 5.0 $\mu A/cm^2$ and 10 kV.

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the best CRT fabricated by the previous contractor (Ref. 2) utilizing a sublinear Zn_2SiO_4:Mn. The low-current-density color appeared an excellent green; however, reference to Figure 8 shows that the color shift passed close to the white area and the colors resulting from intermediate and high current densities were desaturated.

While making measurements on this CRT, the 1x2-inch raster was held on one portion of the screen for several hours. When the raster was expanded later, a bright green 1x2-inch rectangle remained on that part of the screen previously used. This "bright burn" did not fade substantially either during or between periods of excitation and it apparently occurs at the higher current densities. No physical burn of the screen was noted until the current density exceeded 5 $\mu A/cm^2$. Spectrometric and photometric examinations of the burned and unburned portions of the screen were made and the results were as follows:

- The red-emitting superlinear sulfide phosphor was not affected; its luminance, chromaticity and linearity factor were unchanged.
- The green-emitting sublinear gallate was unchanged in chromaticity and linearity factor, but its luminance in the burned area was twice that in the unburned area.
- The gallate emission in the burned portion appeared to have lower persistence.

This bright burn had not been observed on unaluminized screens in the demountable CRT; therefore, 1-inch screens were prepared with the same phosphor mixture where one-half of the phosphor area was aluminized. Exposure of the screens to irradiation at 5 $\mu A/cm^2$ for extended periods failed to produce any trace of bright or dark burn in either portion of the screen.

Coincidentally, a CRT containing sublinear Zn_2SiO_4:Mn mixed with the same superlinear phosphor was also found to produce green "bright burn." Half-aluminized one-inch screens prepared with this phosphor mixture produced a different result: both halves developed "bright burn." Leverenz (Ref. 7) relates "bright burn" to several possible factors, but time has not allowed further investigation into this phenomenon.

Third delivery. -- One 5-inch round SC-5780 type CRT was accepted for the third delivery. This tube was screened with a 2 to 1 mixture of superlinear red-orange emitting sulfide and sublinear yellow-green emitting $NaTaO_3$:Tb. Test data are listed in Table IX and plotted in Figure 8 (CRT No. B1850-4A). The color gamut produced by this screen is about 16 percent less than that obtained with the gallate phosphor, but reference to Figure 8 shows that greater saturation of the colors results from using the tantalate. Furthermore, the tantalate allows greater luminance with a high/low luminance ratio only one-half that of the gallate tube, i.e., greater luminance equalization between low and high current densities. The use of a Nd-glass filter extended the color gamut of this CRT by 14 percent to nearly the values obtained with the unfiltered gallate tube. Reference to the spectra of Figures 10 and 11 shows the effectiveness of the Nd-glass in absorbing the long wavelength Tb peaks and in cutting the short wavelength side of the sulfide emission band.

Finally, it was found that the CRT containing the tantalate phosphor exhibited neither bright nor dark burn and was stable after 2 hours of operation at 5.0 $\mu A/cm^2$.

CONCLUSIONS

The work done on this contract has resulted in finding two new sublinear phosphors which, when mixed with superlinear sulfide phosphors, offer advantages over previous current-sensitive color CRT screens. The two green-emitting phosphors, $K_2O \cdot 6Ga_2O_3$:Mn and $NaTaO_3$:Tb, give excellent sublinear behavior at luminance levels which are quite suitable for use with superlinear sulfide phosphors. $NaTaO_3$:Tb is sublinear at relatively high activator concentrations so that reproducibility is not a problem as with phosphors requiring very low activator concentrations. The tantalate phosphor is the only known nonlinear, lanthanide-activated phosphor and has excellent stability (both luminance and color) under electron beam excitation at high current densities ($>5\ \mu A/cm^2$). The gallate phosphor has shown luminance changes when excited at high current densities, and therefore, further work is needed before this phosphor is as suitable for use in tubes. The use of new sublinear green phosphors has resulted in a reduction in the luminance difference between low and high current density operation.

The use of selective filters has been shown to give some additional improvement in color gamut. Further improvements in color range and contrast by selective filtering would require more extensive work on tailoring filter characteristics to better match the phosphor emission spectra.

It is concluded that any future major improvements in luminance difference, total luminance and color gamut would require improved superlinear phosphors. In

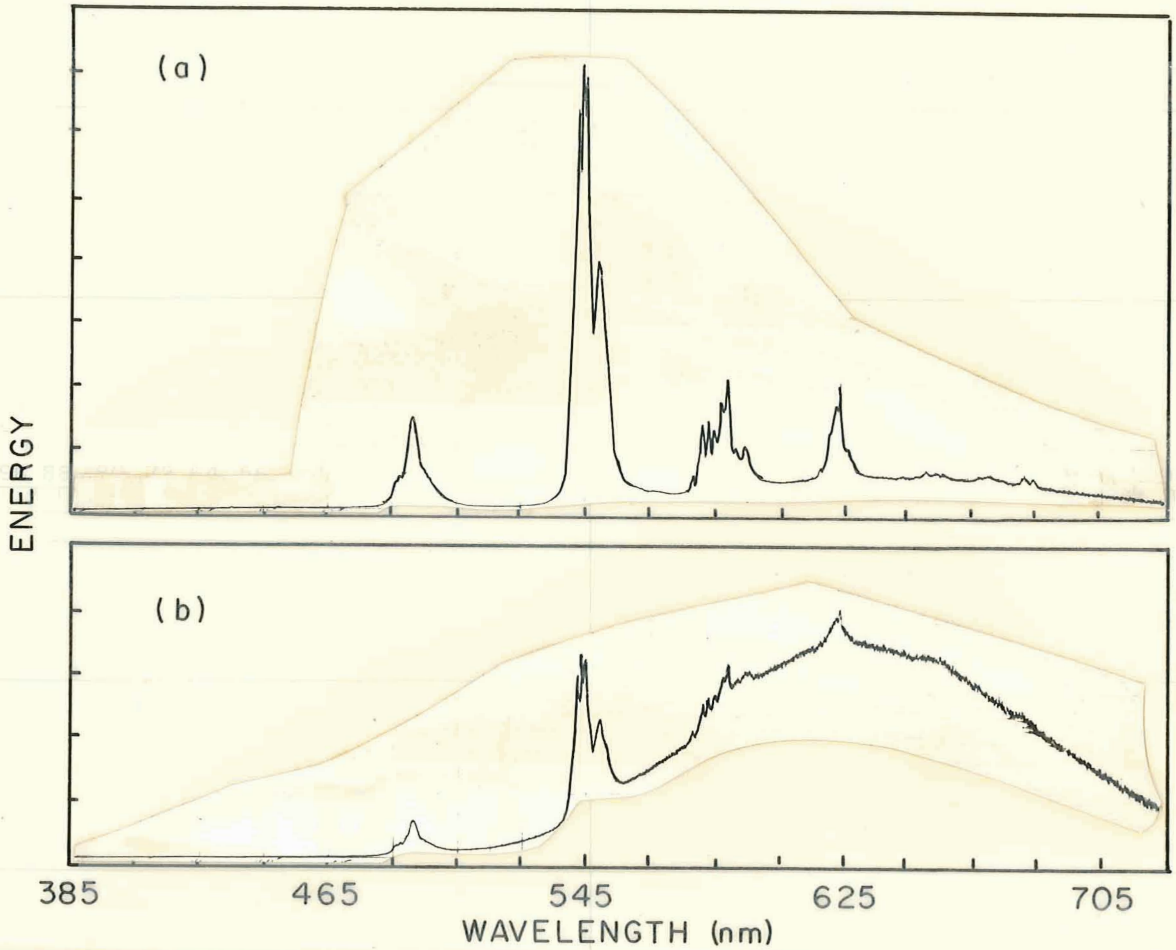

Fig. 10. Cathodoluminescence spectrum from CRT No. B1850-4A operated at (a) 0.1 $\mu A/cm^2$ and 10 kV, and (b) 5.0 $\mu A/cm^2$ and 10 kV.

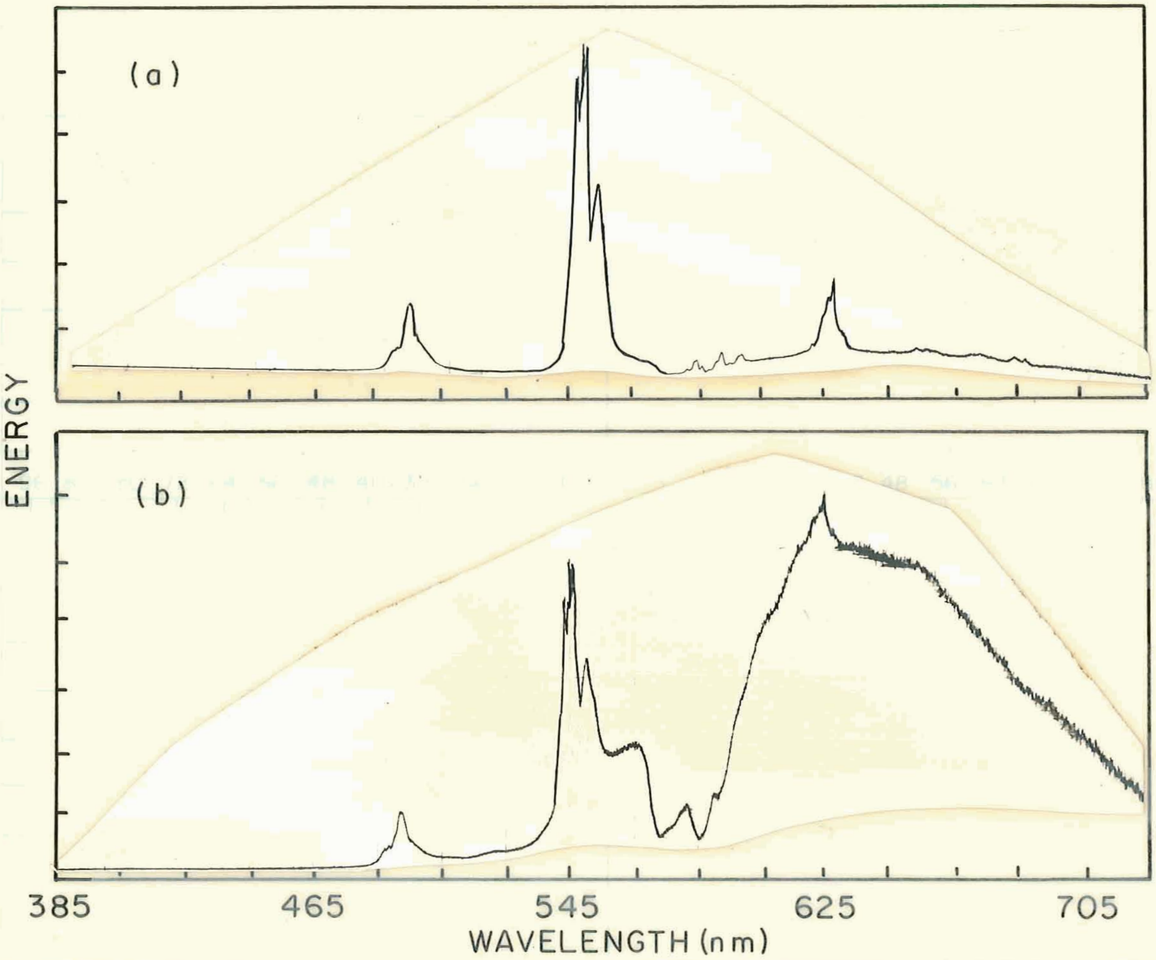

Fig. 11. Cathodoluminescence spectrum through Nd-glass from CRT No. B1850-4A operated at: (a) 0.1 $\mu A/cm^2$ and 10 kV, and (b) 5.0 $\mu A/cm^2$ and 10 kV.

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particular, higher luminance from the superlinear phosphor would permit the use of phosphor mixtures in ratios close to unity thereby enhancing the overall output of the CRT. Superlinear phosphors having more saturated green and red emissions than now available and superlinear phosphors, having saturated blue emission, would permit a wider selection in the directions of color shift desired. In this regard, the probability of obtaining better superlinear phosphors depends to a large extent on a better understanding of the mechanisms leading to superlinear behavior.

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Chromaticity Measurements and Spectral Recording - S. Mosca
CRT Screening - J. T. Ragusin
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NEW TECHNOLOGY APPENDIX

The following are considered to be Reportable Items made in the performance of work under this contract:

A. Title: Phosphors with Sublinear Dependence of Luminance on Current Density.

Page Ref.: 16 to 23.

Comments: Several known phosphors were found to exhibit sublinear luminance-current density behavior. $K_2O \cdot 6Ga_2O_3$:Mn and $NaTaO_3$:Tb were the only ones producing green emission comparable in intensity and sublinearity to that of previously reported sublinear Zn_2SiO_4:Mn.

B. Title: Selective Absorption Filters for Current-Sensitive Polychromatic Single-Gun CRTs.

Page Ref.: 3 to 4; 22 to 34.

Comments: Absorption filters which had been evaluated with various polychromatic CRTs were applied to current sensitive CRT screens and were found to aid in expanding the chromaticity gamuts.