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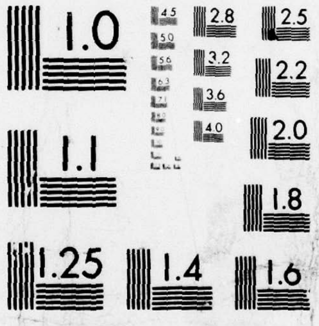

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EVALUATION OF MICROENCAPSULATED PHOSPHORS

R. B. Reif, O. A. Ullrich, T. S. Shilliday,
and P. E. McCrady

The United States Air Force
Air Force Materials Laboratory
Air Force Systems Command

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Final Report July 1978 - February 1979

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To determine how encapsulation affects the light output of electroluminescent phosphors, direct comparisons were made between plain and microencapsulated phosphors of the same control lot with nominal 0.5, 1.0, and 3.0-micron walls. Light output was normalized with respect to the amount of phosphor as a general procedure.

Examination under magnification revealed that the encapsulating coatings formed diametric protrusions on the phosphors; however, theoretical studies subsequently

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20. ABSTRACT (Continued)

indicated that the conical shaped ends probably would not act as light tubes to enhance the apparent light output. Factors such as coating thickness, phosphor composition and concentration, spectral emission, and origin of the emission were studied. Shifts of emission wavelength and emission peaks were noted with decreasing temperature down to about - 265C for both UV and electrical excitation. Encapsulation had no significant effect on the output of UV excited phosphors.

The program was concluded with work to confirm the results of the initial AFML work which had indicated that microencapsulation enhanced the light output of phosphors. The original results were not confirmed although the same procedures and material lots were used.

PREFACE

Technical Report No. AFML-TR-79-4071 is the final technical report on USAF Contract No. F33615-78-C-5160. The report concerns work done at Battelle Columbus Laboratories in connection with a program on "Basic Studies of Encapsulated Electroluminescent Materials" which was conducted for the Air Force Materials Laboratory under Mr. Bill Dobbs with the Systems Acquisition and Logistics Support Branch of the Systems Support Division.

The work was conducted in the Engineering Physics and Electronics Section at Battelle with Mr. R. B. Reif leading the work on the project. Mr. O. A. Ullrich conducted spectrophotometric and cryogenic studies and Mr. T. S. Shilliday made the theoretical studies. Mr. P. E. McCrady constructed special apparatus and conducted most of the laboratory work on the project. Analytical work was performed by other specialists at Battelle.

The assistance of Mr. Bill Dobbs and Mr. Sidney Allinikov of the Air Force Materials Laboratory, Air Force Systems Command, was greatly appreciated in connection with the planning and evaluation of the results of the work done on this program.

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SECTION I

INTRODUCTION

A study was begun on July 1, 1978, to validate that microencapsulation enhances electroluminescent properties of ZnS:Cu phosphors, elucidate the mechanism of enhancement, and optimize the encapsulating coating to obtain maximum brightness and operating life. The studies were completed on February 28, 1979. This report covers the experimental, analytical, and theoretical studies that were conducted on this program.

SECTION II

SUMMARY

A comprehensive study was conducted to determine how encapsulating coatings affect the light output of electroluminescent phosphors. Factors such as coating thickness and conformation, phosphor composition and concentration, and spectral emission and brightness were studied; and emission sites were examined microscopically. Insofar as possible, direct comparisons were made between plain phosphors and microencapsulated phosphors of the same control lot with nominal 0.5, 1.0, and 3.0-micron walls. Light output was normalized with respect to the amount of phosphor as a general procedure in these studies.

The laboratory examinations revealed that the encapsulating coatings formed diametric protrusions on the particles, and a theoretical study subsequently was made to determine if the resultant conically shaped ends might act as light tubes to enhance the apparent light output.

Spectral emission was measured under cryogenic conditions at temperatures down to about -265 C for both UV and electrical excitation. Shifts of emission wavelength and emission peaks were noted with decreasing temperature in both the plain and encapsulated phosphors.

The program was concluded with work to confirm the results of the initial work at the AFML which had indicated that microencapsulation enchanced the light output of phosphors. Materials from the same lots used in the original work were processed in the same method used in the original work, but the original results were not confirmed.

The results of these studies are reported in detail along with conclusions based on the work.

SECTION III

EXPERIMENTAL PROGRAM

Laboratory studies were conducted to determine how encapsulation affects the light output from electroluminescent materials and to develop information that eventually might be used to improve and maximize the light output and operating life of electroluminescent materials and devices. Chemical and physical properties of the plain and encapsulated phosphors first were measured and compared to ascertain what macroscopic and microscopic transformations occur as a result of encapsulation. Emission characteristics then were measured under controlled conditions and correlated with various parameters such as wall thickness and phosphor density in films.

Information developed in the laboratory studies subsequently was applied to guide the theoretical studies in setting up likely enhancement mechanisms.

Physical Characteristics of Particles

Samples of plain and encapuslated phosphor from the same batch of Sylvania 723 Green Lot 166-33B* were examined and analyzed to characterize the materials and to identify differences. Nominal coatings of 0.5, 1, and 3-microns were applied by Capsulated Systems, Inc., Yellow Springs, Ohio. The phosphors were photographed under magnification to show significant features produced by the wall material, and the wall thickness was determined by observation and by calculation based on weights. Emission sites on individual particles also were examined under magnification and the composition of the particles was determined by spark emission spectroscopy.

Wall Thickness

To determine the thickness of the coatings, the encapsulated powders were shadowed with a thin film of vacuum-deposited aluminum to make the coatings more visible. Figures 1 through 4 are photographs showing the plain phosphor and encapsulated phosphors with nominal 0.5, 1, and 3-micron walls, respectively, under magnification of 500 X. Although not readily apparent in Figure 2, the nominal 0.5-micron walls could be observed by focusing the microscope and appeared to be somewhat heavier than one micron. The nominal 1-micron and 3-micron walls were correspondingly thicker and highly variable. The encapsulated particles characteristically had diametric protuberances of coating material which increased in size dramatically with coating thickness. The protuberances probably are caused by rupturing of strings of material consisting of a mixture of the particles and the coating material. Apparently the

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* Purchased from GTE Sylvania Incorporated under Contract No. F33657-77-A-0003 for PRAM Program Office

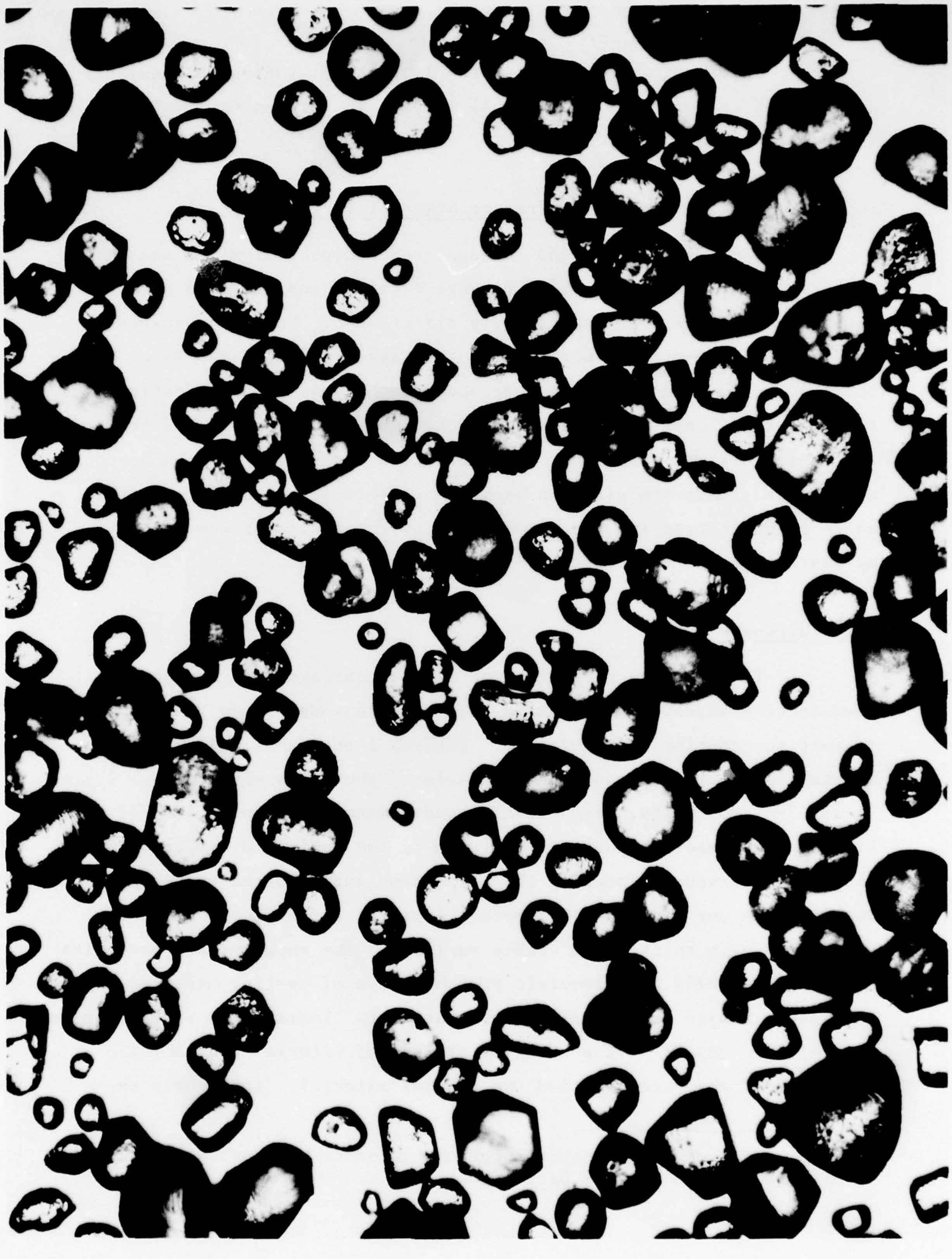

Figure 1. Plain Phosphor - 500X

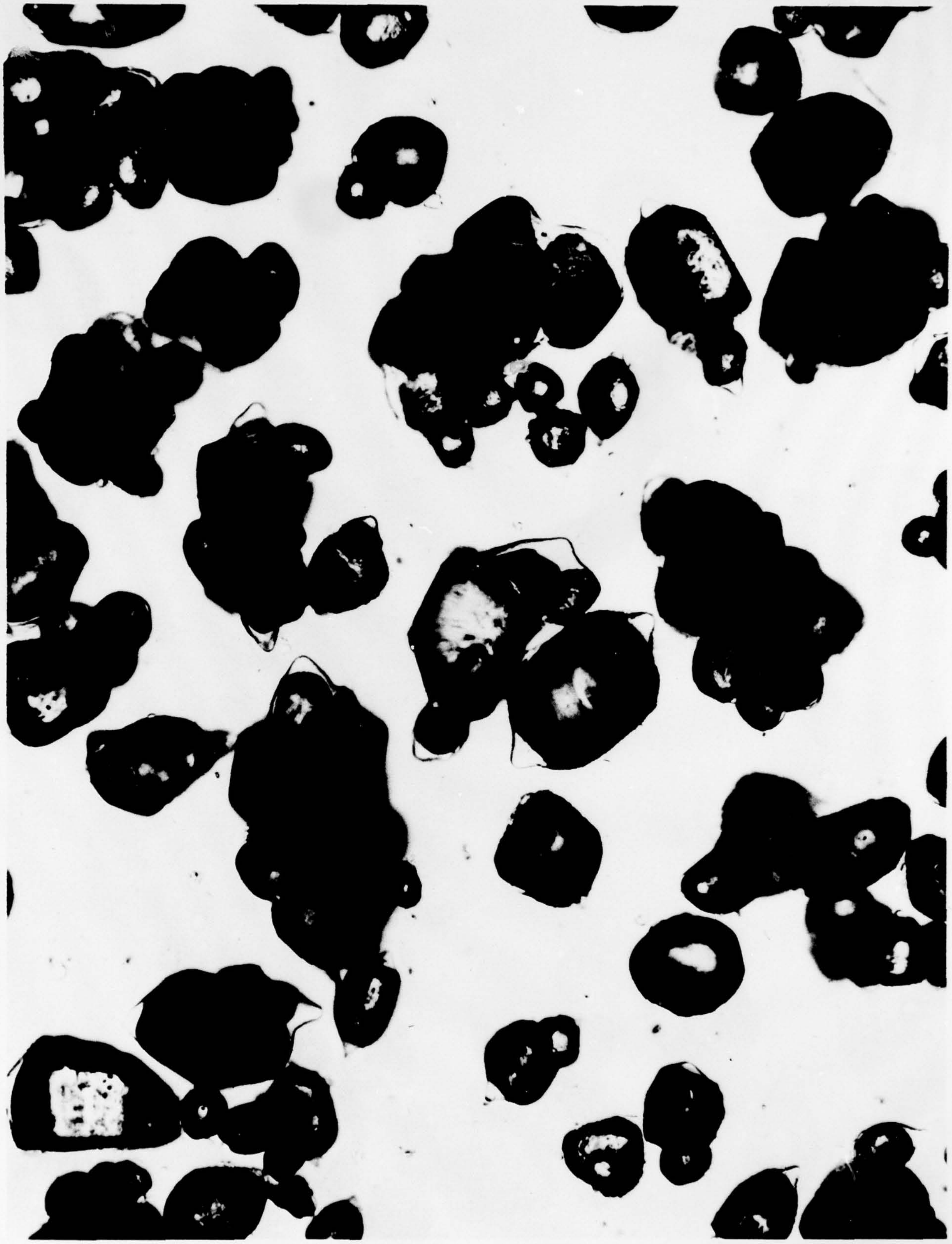

Figure 2. Phosphor With Nominal 0.5-Micron Wall - 500X

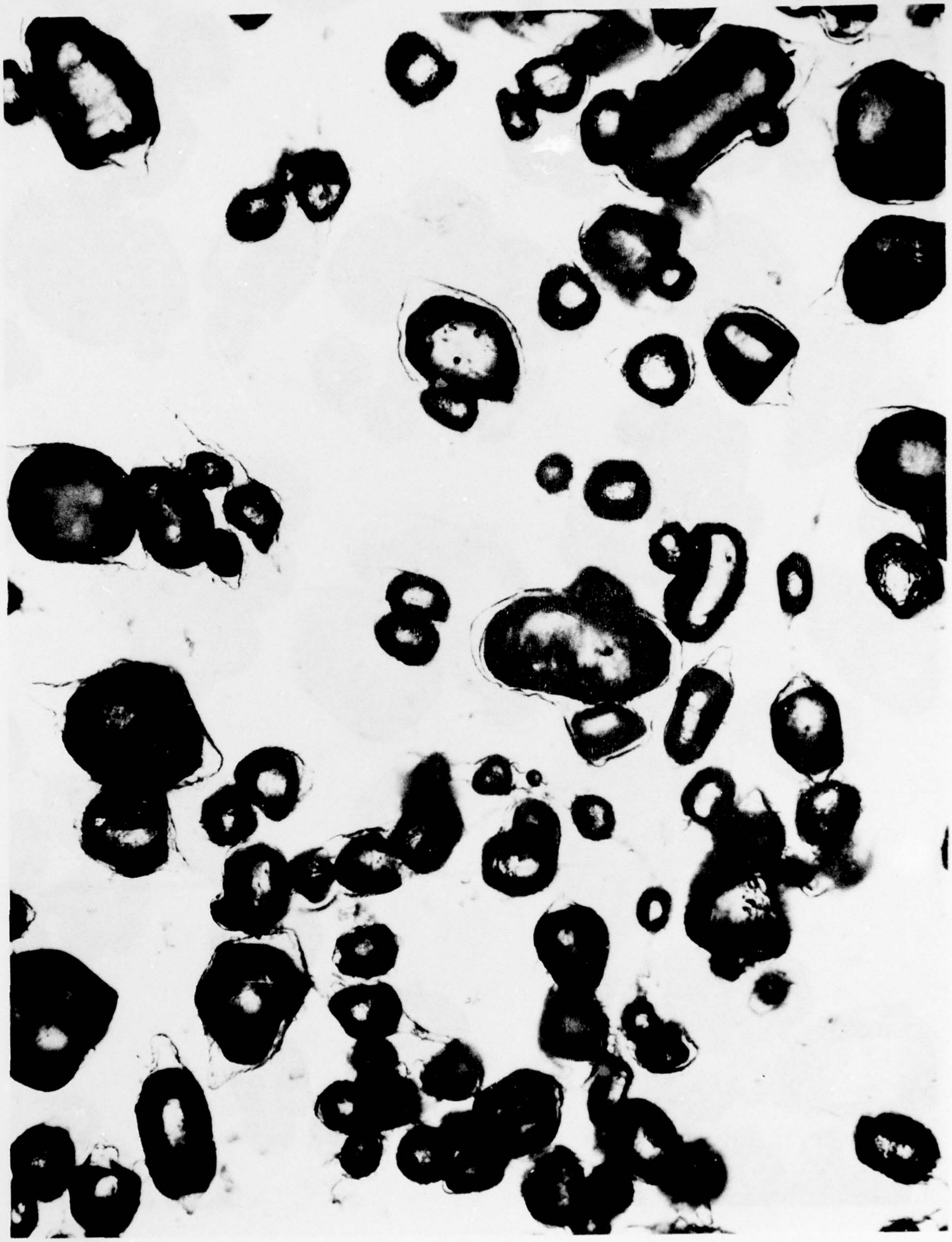

Figure 3. Phosphor With Nominal 1-Micron Wall - 500X

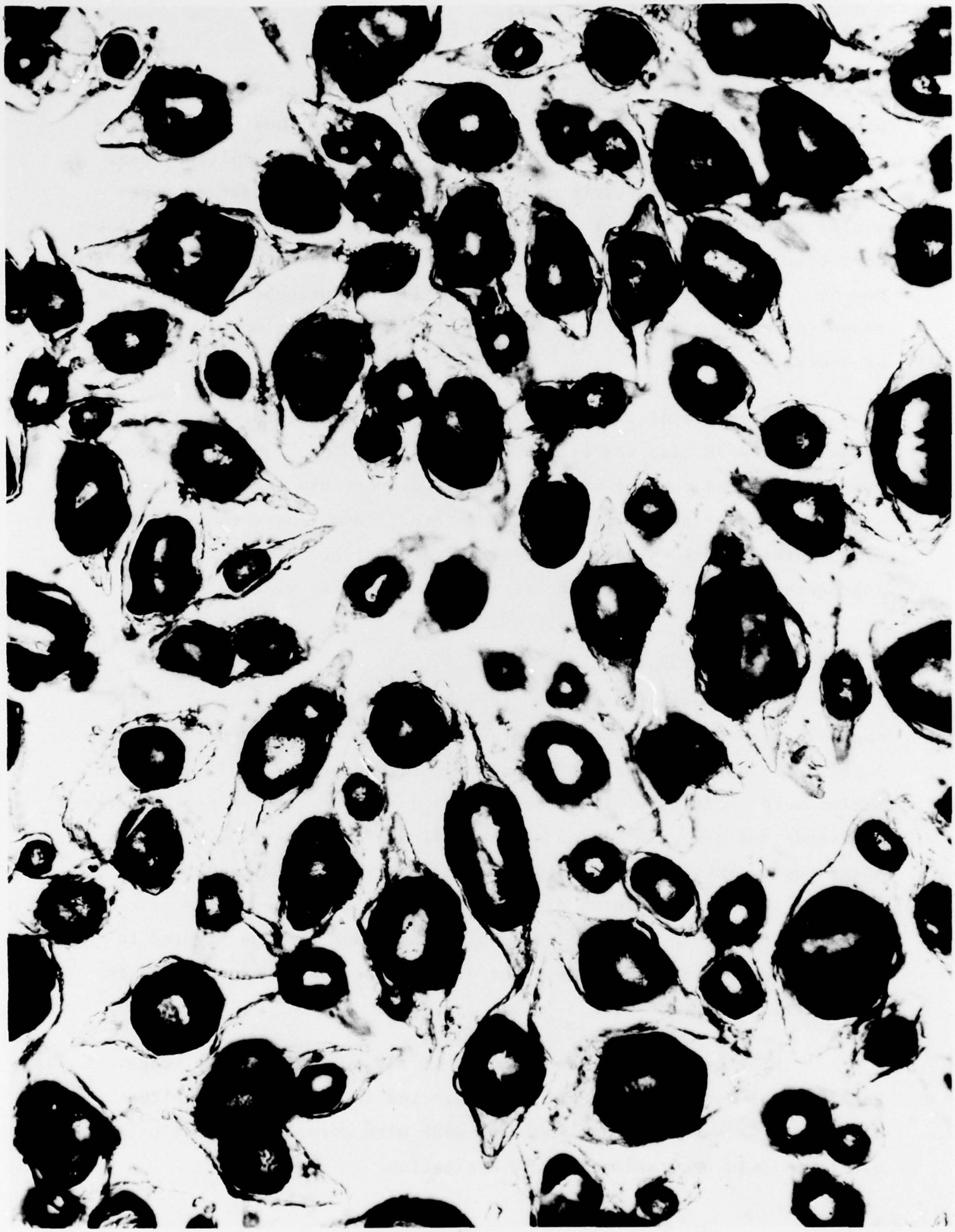

Figure 4. Phosphor With Nominal 3-Micron Wall - 500X

material either coalesced during the encapsulating process, or the phosphor particles were not thoroughly dispersed as they were encapsulated and they were stirred violently to break up the resultant mass. The large number of particle agglomerates that can be observed especially in the material with 0.5-micron and 1-micron walls tends to support this conclusion. The reduced surface area presented by agglomerates may be a factor in producing the heavy walls and protuberances but the amount of coating material present in all of the fractions appears to be excessive.

A sample of the Sylvania Green 723 Phosphor Lot 166-33B encapsulated by 3M also was examined and photographed at 500X. Figure 5 shows that the coating wall is about 2 microns and that the encapsulated phosphor particles are agglomerated. Some extraneous formations of the urea formaldehyde encapsulating material are visible, but protuberances were not present or at least not readily visible.

Light-Emission Sites

Light emission from individual particles was examined under magnification to determine how emission is affected by encapsulation. A pair of electrodes was set up under a microscope and individual particles were excited by electrical fields and by UV. After trying various electrode designs, the device shown in Figure 6 was developed with two sharp-edged disks approximately 1.27 cm (1/2 inch) in diameter. The 0.025-cm (0.010 inch) thick disks were mounted on one end of a pair of metal arms. One arm was fixed while the other arm was pivoted to permit changing the gap between the disks. The disks were rotated to move particles in the gap.

The Lucite base was designed to fit on a microscope stage. Particles of various diameters were inserted in the gap between the disks, and were examined at 430X and 860X with normal illumination, electric-field excitation, and UV excitation.

Figure 5. Phosphor With 3M Coating

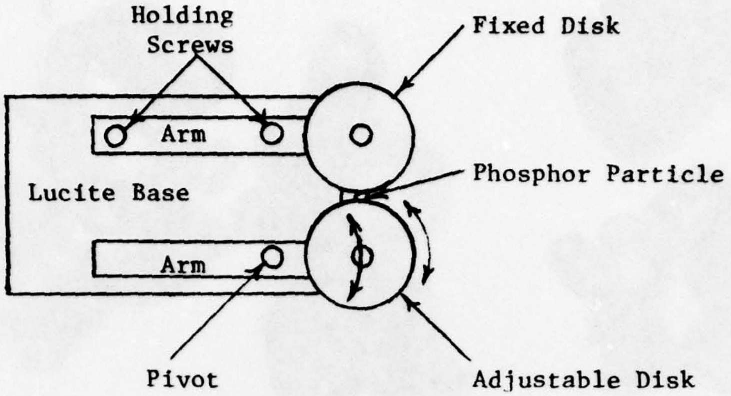

Figure 6. Adjustable Electrodes For Microscope Stage

With an applied potential of 200 volts at 20 kHz, typical high light-emission spots occurred near the electrodes. However some emission occurred over the whole particle. A somewhat higher level of emission was produced over the whole particle with UV excitation. In general, the visually observed emission from the plain phosphor particles was slightly brighter than the emission from a comparably sized encapsulated particle; however, the emission was more uniformly distributed over the surface of the encapsulated particles.

A number of interesting phenomena were observed including bright e.l. emission along cracks in particles, dark spots from which no e.l. or U.V. excited emission occurred, and firey sparkler-like disintegration of plain phosphors in electrical fields. Disintegration was not observed in encapsulated particles. Time-exposure photographs were made of some of the excited phosphors with Polaroid No. 47 High Speed Film; however, the quality of the photographs was poor. The disintegration phenomena could not be photographed because the amount of light produced by a single particle was too low.

Weight Analysis

Measurement of the true phosphor composition in the three encapsulated batches was a high-priority task. At first, removal of the coating with solvents was attempted since the solvent-stripped material would be useful in other analytical studies. Various solvents and proprietary solvent mixtures were tried without success, although ultrasonic agitation in acetone appeared to remove some of the coating. Finally, to achieve complete removal of the coatings, the encapsulated phosphors were heated to about 538 C (1000 F) for 30 minutes to burn off the coatings. The measured weights determined by this method are compared with the calculated weights in Table 1.

Table 1.

Comparison of Measured and Calculated Phosphor Weights

Nominal Coating Wall, microns	Phosphor Weight, percent	
	Measured*	Calculated**
0.5	97.3	97.2
1.0	93.9	94.4
3.0	84.4	83.3

* Average of three determinations

** For the purpose of calculation, the density of the phosphor was assumed to be 4.1(1) and the density of the coating was assumed to be 1.05(2). (See Appendix 1)

The agreement between the calculated and measured phosphor content generally was good.

Composition of Particles

Six samples including two samples of plain and various forms of encapsulated Sylvania 723 Green Phosphor Lot 166-33B were analyzed by spark-source mass spectroscopy (SSMS) to determine if elemental changes occurred in the phosphor composition as a result of the encapsulating wall or the encapsulating process. In addition to the plain and encapsulated phosphor with a nominal 0.5-micron coating, a sample (59-28) of phosphor from which the wall had been removed* and a sample of phosphor which had been processed through the microencapsulating system without applying a wall were analyzed. The encapsulated phosphor and the latter two samples were prepared by Capsulated Systems, Inc., Yellow Springs, Ohio.

Table 2 shows only the elements detected at significant levels by the SSMS analyses. Repeat analyses were made on the plain and encapsulated phosphors to determine reproducibility and/or variability in the composition. Within the accuracy of the analytical technique, the Na, Mg, S, Cl, Zn, and Ba concentrations in all the processed samples were comparable to the concentrations in the original plain phosphor. The decrease in Mg in Sample 59-28 may not be significant because the phosphor was treated with materials not normally used in the encapsulating process. Only the Si, which increased from about 7 to 50 ppm to about 1500 to 2000 ppmw, showed a significant increase as a result of adding the coating. Silica is used to control the viscosity in the microencapsulation process. The Si concentration in the phosphor processed without the wall was comparable to that in the plain phosphor. This confirms that the Si in the phosphor with the 0.5-micron walls is in the wall as was indicated also by the SSMS analysis of sample 59-28 in which the encapsulating wall was removed with a solvent.

Repeat runs on the plain and encapsulated phosphors suggest that the Cu concentration may be variable. Based on these analyses, however, the encapsulation process does not appear to change the basic composition of the phosphor significantly although the coating wall contains a significant amount of Si.

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* The wall was not hardened during the encapsulation process.

Table 2.

SSMS Analysis of Sylvania 723 Green Phosphor Lot 166-33B

Element	Concentration, ppmw					
	Plain		Coated 0.5-Micron Wall		Sample 59-28 (Wall Removed)	Processed Without Wall
	1	2	1	2		
Na	15	30	50	30	15	20
Mg	500	500	500	500	250	500
Si	7	7to50	1500	2000	<4	2
S	Major	Major	Major	Major	Major	Major
Cl	40	50	40	30	30	20
Cu	1500	600	1500	300	200	400
Zn	Major	Major	Major	Major	Major	Major
Ba	300	400	600	400	400	200

Composition of Coating

The coating on the Sylvania 723 Green Phosphor Lot 166-33B was identified as an oil modified polyurethane resin in a prior program conducted for the PRAM Program Office on Contract No. F33657-77-A-0003. The coating material was extracted by soaking the encapsulated phosphor in MEK and the identification was made by IR spectroscopy using a Perkin-Elmer Model 521 Spectrophotometer. The work is reported on page 45 of the Final Report on "Electroluminescent Lighting Systems", October 1, 1977, to March 31, 1978.

Light Emission

The effect of the coating wall on the light-output level and spectral emission of the phosphors was studied carefully. The light output was related directly to the amount of phosphor in the test cell. Also, the effect of low temperatures on both photoluminescense and electroluminescense was studied to determine if the encapsulating material or encapsulating process affected the basic character of the phosphor.

Equidensity Cells

In order to compare the effect of the encapsulating wall on the light output from the phosphor, test cells were made with the phosphors with nominal 0.5, 1.0, and 3.0-micron walls. The light output was normalized by relating it to the actual weight* of phosphor in a constant size cell. The test cell was 0.635 cm (0.25 inch) in diameter and 0.009 cm (0.0037 inch) thick formed with two layers of pressure-sensitive tape between two Nesa-glass electrodes. The phosphor powder was doctored into the cell and a small amount of mineral oil was bled into the cell to fill voids between the particles. Nesa glass electrodes were used initially on both sides of the cells so that the phosphor could be excited with UV light** through the back window while measuring the luminescence from the front window. However, the resultant luminescent emission*** from the front of the cell decreased with cell thickness. Doubling the cell thickness from 0.0045 cm (0.0018 inch) to 0.009 cm (0.0037 inch) cut the relative brightness**** of the emission peak in half while the amount of plain phosphor in the cell increased from 0.0055 gm to 0.0111 gm. Increasing the cell to 0.0140 cm (0.0055 inch) decreased the relative brightness of the emission peak to less than one third of the original brightness while the amount of phosphor in the cell increased to 0.0164 gm. Obviously, the UV light and/or the emitted light was absorbed by the phosphor. Frontal illumination at an angle

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* Based on measured weights

** Long wave length Blak-Ray Model 100 lamp made by Ultra-Violet Products, Inc., San Gabriel, Ca.

*** Measured with an EGG Model 555 Spectroradiometer

**** Actual brightness; not normalized by phosphor weight of about 30 degrees to the surface of the window subsequently was evaluated in the same cells. The relative brightnesses of the emission peaks and total emissions were about the same for all three cells; consequently, frontal illumination was selected for comparing emission from the encapsulated phosphors with various wall thicknesses.

Subsequently, the 0.009-cm (0.0037 inch)-thick cell was filled with about 0.0117 gm of plain phosphor, 0.0115 gm of 0.5-micron-wall phosphor, 0.0090 gm of 1.0-micron-wall phosphor, or 0.0068 gm of 3.0-micron-wall phosphor. The relative brightness of the emission peak at 480 to 490 nm was measured with UV excitation and with electrical excitation at an applied potential difference of 300 volts at 20 kHz with the results shown in Table 3.

Table 3.

Comparison of Equidensity Cells

Phosphor	Weight, gm		Relative Brightness[a]			
			EL		Photoluminescence	
	Total	Phosphor	Actual	Normalized/mg	Actual	Normalized/mg[b]
Plain	0.0117	0.0117	267	22.8	215	18.4
0.5-Micron Wall	0.0115	0.0112	95	8.5	262	23.4
1.0-Micron Wall	0.0090	0.0084	43	5.0	261	30.9
3.0-Micron Wall	0.0068	0.0057	22	3.8	189	33.5

(a) No units, for comparison only

(b) Relative brightness per milligram of phosphor

Just the 0.5-micron wall decreased the brightness of the emission peak by electroluminescent excitation to about one third of the brightness of the emission peak with plain phosphor. Doubling and tripling the wall thickness produced corresponding decreases in brightness of the emission peak. Normalizing the relative brightness on the basis of milligram of phosphor in each cell improved the results only slightly. Surprisingly, the brightness of the emission peak produced with UV excitation was greater in cells with two of the encapsulated phosphors than in cells with the plain phosphor and the normalized brightness increased with thicker walls. This effect suggests that encapsulation might enhance the output of fluorescent powders when used in cascade systems that are driven by a layer of electroluminescent material.

The effect of cell thickness on the electroluminescent emission of plain phosphor also was determined by testing three different cells with applied voltage proportional to the cell thickness to produce the same field strength across the cells. The cells were made without oil. Unexpectedly the light output was highest from the thickest cell ranging from an emission peak of 28.2 in a 0.0045-cm (0.0018 inch) cell* to 59.1 in a 0.0094-cm (0.0037 inch) cell** and 88.1 in a 0.0140-cm (0.0055 inch) cell***. Normalization of the data based on the milligrams of phosphor in each cell then resulted in a much narrower spread from 51.3 units per mg in the thin cell to 53.2 and 53.7 units per mg in the respectively thicker cells.

To determine if absorption by the encapsulating coating is a factor in the light reduction, a glass microscope slide with a 0.3-mil coating of polyurethane varnish, which was equivalent to the total urethane coating that would be on the phosphor in the test cell, was placed over a cell with plain phosphor. The phosphor then was excited by a potential difference of 300 volts at 20 kHz. When the effect of the glass was eliminated, the polyurethane coating reduced the emission

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* At 140 volts and 20 kHz

** At 280 volts and 20 kHz

*** At 420 volts and 20 kHz

by only about 0.5 percent. This does not account for the losses already measured. Since the SSMS analysis of the encapsulated phosphors showed an increase of 1500 ppmw of silica, silica in the form of Microcel was added in the polyurethane varnish to approximate the composition of the encapsulated phosphors. Although the resultant 14 percent reduction in the spectral emission was significant, the reduction was less than generally produced by the equivalent amount of coating material on the encapsulated phosphors. This result suggests that the effect of the encapsulating coating is electrial rather than optical.

Emission at Liquid-Nitrogen Temperatures

Emission measurements at low temperatures first were made in a system cooled with liquid nitrogen. A 1.9-cm (3/4-inch)-diameter test cell with a Nesa glass front electrode was mounted on an aluminum block bolted to a metal plate in the bottom of a special Dewar flask. The cell was insualted with plastic foam and foil-covered fiberglass, leaving a window at the front of the cell. The cell and insualtion were enclosed in a polyethylene-walled chamber. A UV Blak-Ray lamp about 26.7 cm (10.5 inches) in front of the cell was connected to a window in the polyethylene wall with aluminum foil. The emission from the cell was measured with a fiber-optic probe on an EGG Model 555 Spectroradiometer about 3.8 cm (1.5 inches) from the face of the cell. Prior to cooling, the polyethylene chamber was flushed with dry nitrogen to exclude moisture and thereby prevent water condensation on the cell window and probes at the cryogenic temperatures.

Spectral emission was measured from plain Sylvania 723 Green Phosphor Lot 166-33B and from the encapsulated phosphor with a nominal 0.5-micron wall. A 0.0094-cm (0.0037 inch)-thick cell was filled with 0.1147 gm of plain phosphor or with 0.1180 gm of 0.5-micron-wall encapsulated phosphor which is 97.3 percent phosphor and contains about 0.1148 gm of phosphor. No oil was added to the cells to avoid effects that might be introduced by freezing the oil. Spectral emission from each cell was measured at room temperature (21C) and after the cell was cooled to about -152C with liquid nitrogen in the Dewar. Emissions produced by UV excitation and by electrical excitation with an applied potential difference of 350 volts at 20 kHz were measured for each cell.

Figure 7 shows that the spectral emission of the plain phosphor under UV excitation peaked at about 470 nm at room temperature. The emission peak shifted to about 440 nm and increased at -152C; however, the overall light output decreased at -152C. The emission peak with electrical excitation shifted in the same manner from about 460 nm to 450 nm, but both the brightness of the emission peak and the overall light emission decreased.

Figure 8 shows the spectral emission of the encapsulated phosphor with nominal 0.5-micron walls. The emission of the encapsulated phosphor with UV excitation was identical to that of the plain phosphor in Figure 7 at room temperature and at -152C. However, the emission peak of the encapsulated material with electrical excitation was only about half of the peak of the plain phosphor at room temperature and only about one fourth of the peak at -154C. The slightly lower temperature may have exaggerated this difference somewhat; however, the shifts in the peaks were about the same for the electrically excited plain and encapsulated phosphors. The fact that the encapsulation reduces the electroluminescence and not the UV luminescence strongly indicates that the loss of electroluminescence produced by encapsulation is essentially the effect of the capsule wall on the electrical field. Absorption of light by the wall does not appear to be a factor.

Emission at Liquid-Helium Temperatures

To achieve still lower temperatures, the cryogenic system was rebuilt completely to use liquid helium as the cryogen. The cryostat basically was two concentric thermally insulated chambers with liquid helium in a 1000-ml vacuum flask inside a container with 5-cm

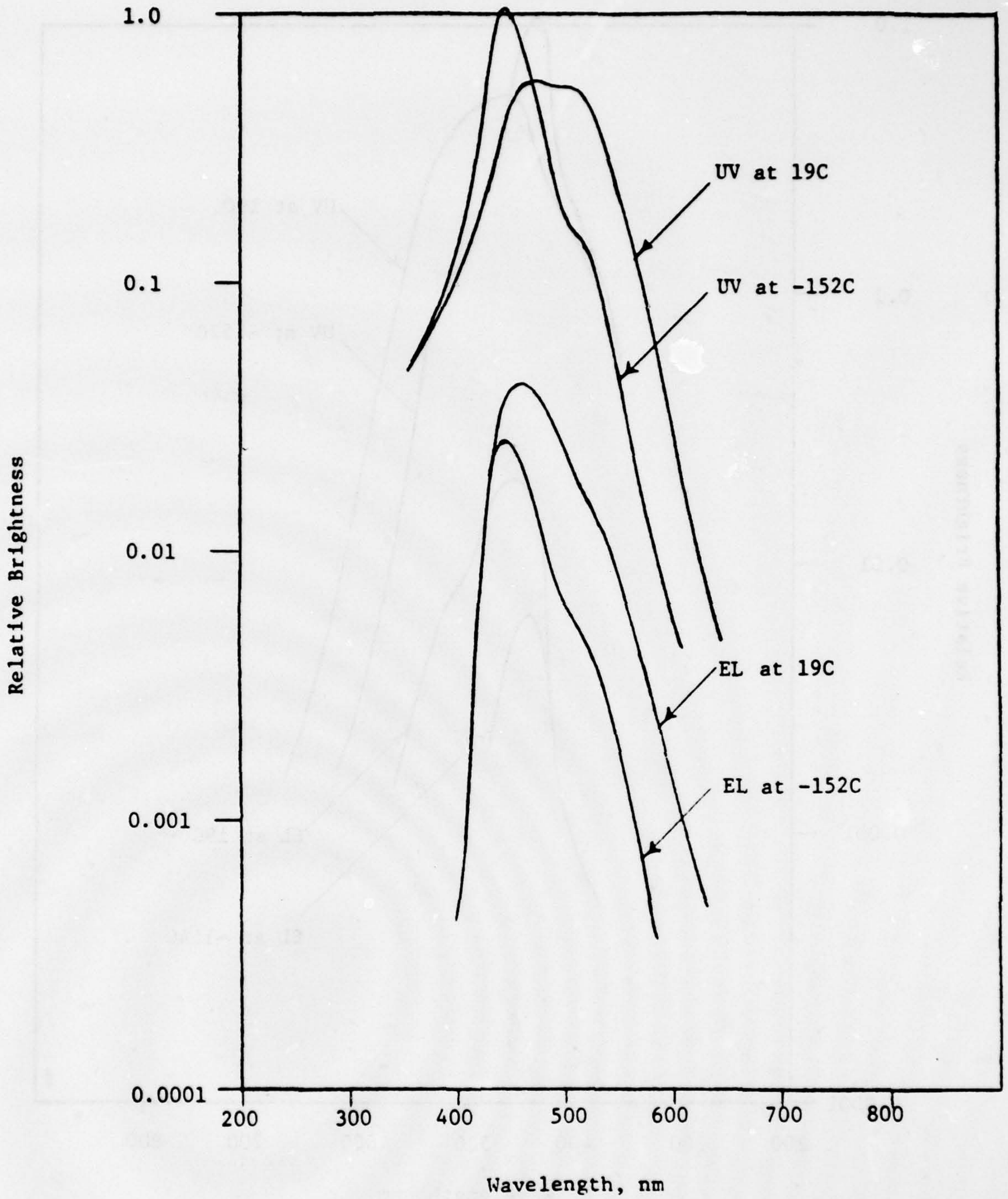

Figure 7. Spectral Emission of Plain Sylvania 723 Green Phosphor Lot 166-33B

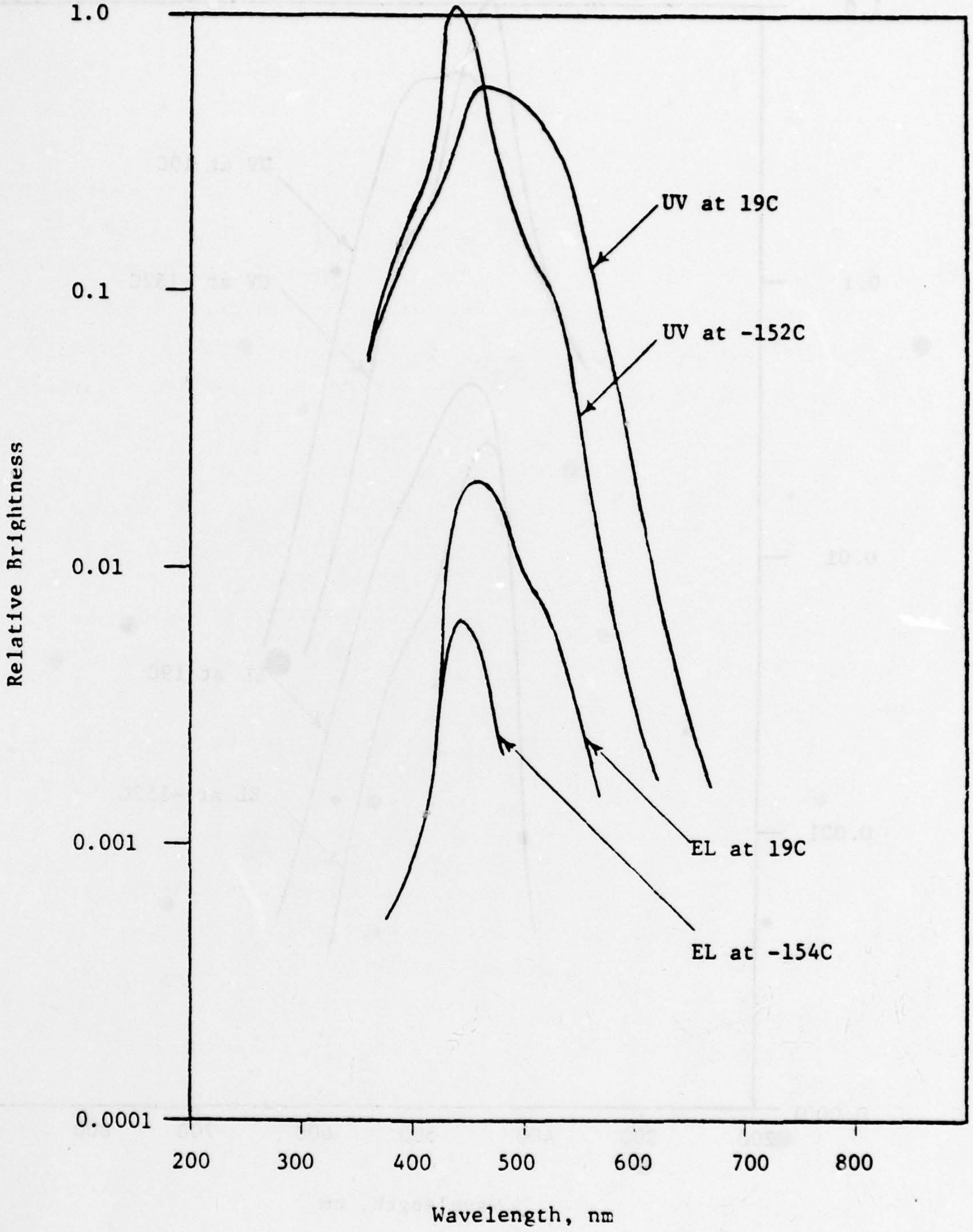

Figure 8. Spectral Emission of Encapsulated Sylvania 723 Green Phosphor tot 166-33B with 0.5-Micron Wall

(1-7/8 inch) Styrofoam walls filled with liquid nitrogen. The test specimen was placed inside a small vacuum tight chamber on the end of a thin-wall stainless steel tube which enclosed separate sets of 0.64-cm (1/4 inch) quartz rods to deliver the UV radiation to the test sample and to return the fluorescent radiation to the EGG Model 555 Spectroradiometer. The power lead and the wires to copper-Constantan Type T thermocouples in the Nesa-glass cover and in the back of the test cell were brought out through vacuum seals on the outer end of the tube along with the quartz rods. Figure 9 shows the disassembled apparatus, and Figure 10 is a sketch of the apparatus assembled with the test chamber in the liquid-helium chamber.

Photoluminescence. The spectral emissions produced by UV excitation of the various phosphor specimens were measured at temperatures down to about -265 C. The phosphors all were from the master lot of plain Sylvania 723 Green Phosphor Lot 166-33B and samples of the encapsulated phosphor with nominal 0.5, 1.0, and 3.0-micron walls. Spectral emission curves for these materials with UV excitation at temperatures of about 22C, -200C, and -265C are shown in Figures 11 to 14.

The emissions from the plain and encapsulated samples were essentially the same. Typically, the broad emission band peaked at about 460 nm at 22C. When the temperature was reduced to about -200 C, the emission band became narrower and the peak emission increased and shifted to about 440 nm. As the temperature was decreased further to -267C, the peak emission decreased but the peak remained at about 440 nm.

The emission from the encapsulated phosphor with 1.0-micron walls was measured at wavelengths longer than 700 nm; these data are plotted in Figure 15.

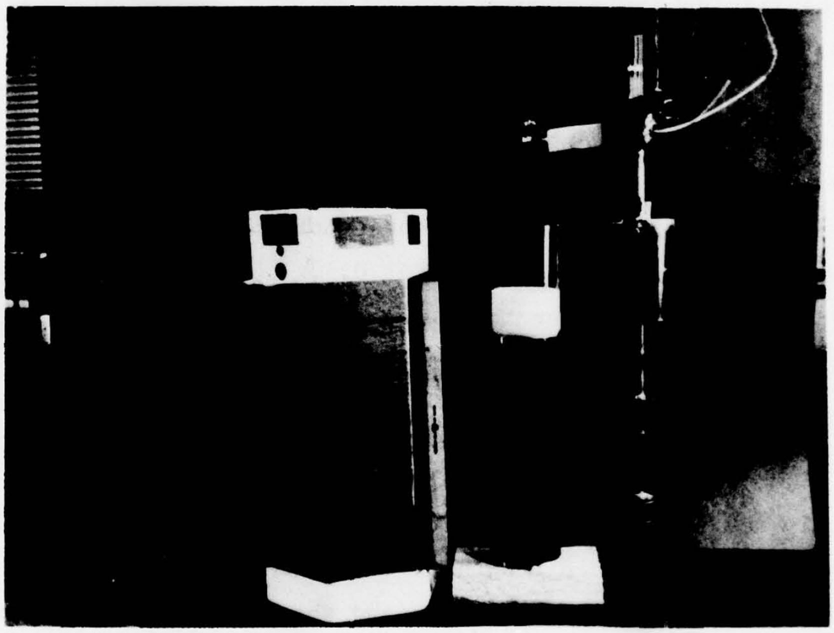

Figure 9. Components of Helium Cryogen Test Apparatus

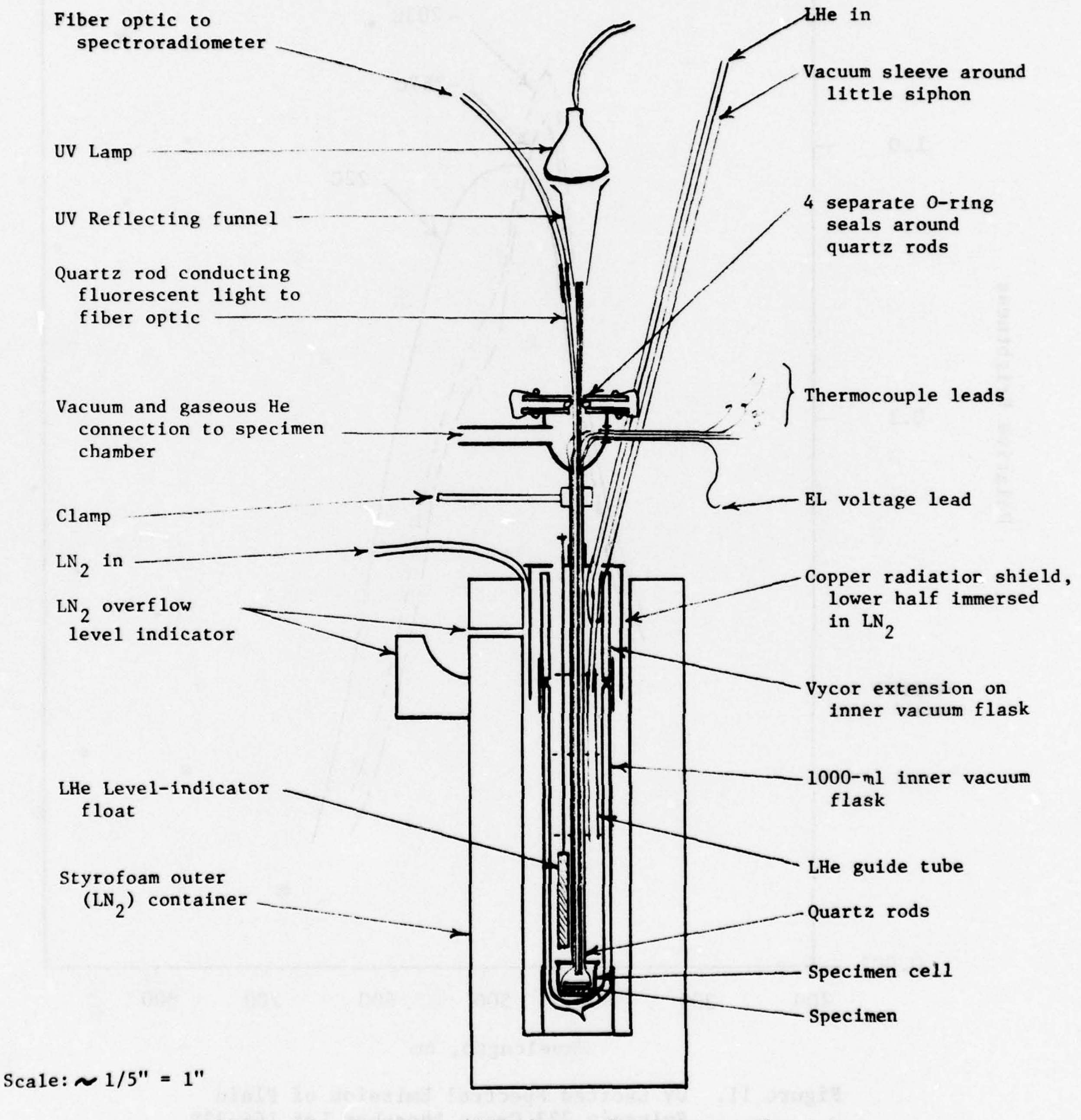

Figure 10. Cryostat and Equipment for Spectroradiometer at Liquid Helium Temperatures

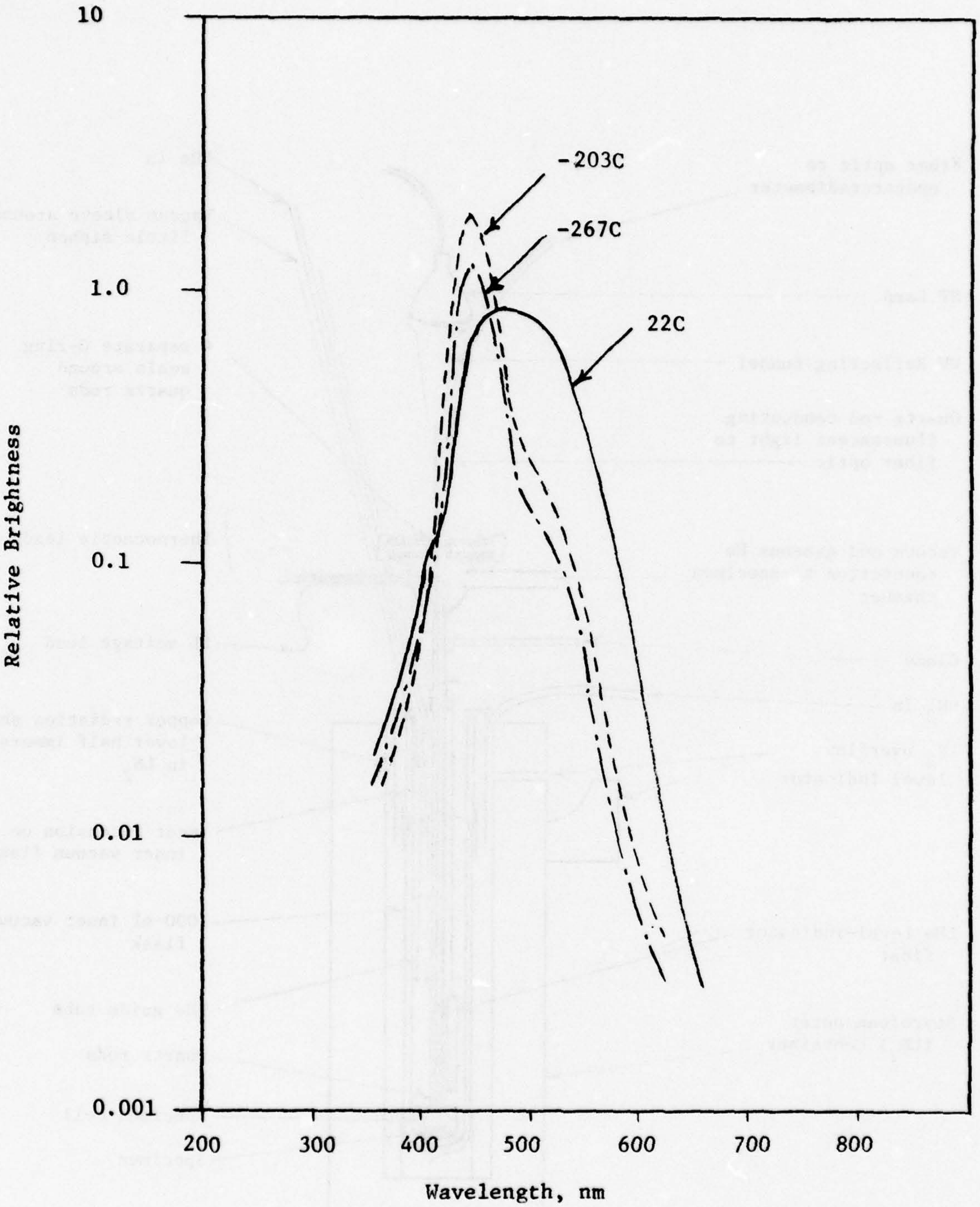

Figure 11. UV Excited Spectral Emission of Plain Sylvania 723 Green Phosphor Lot 166-33B

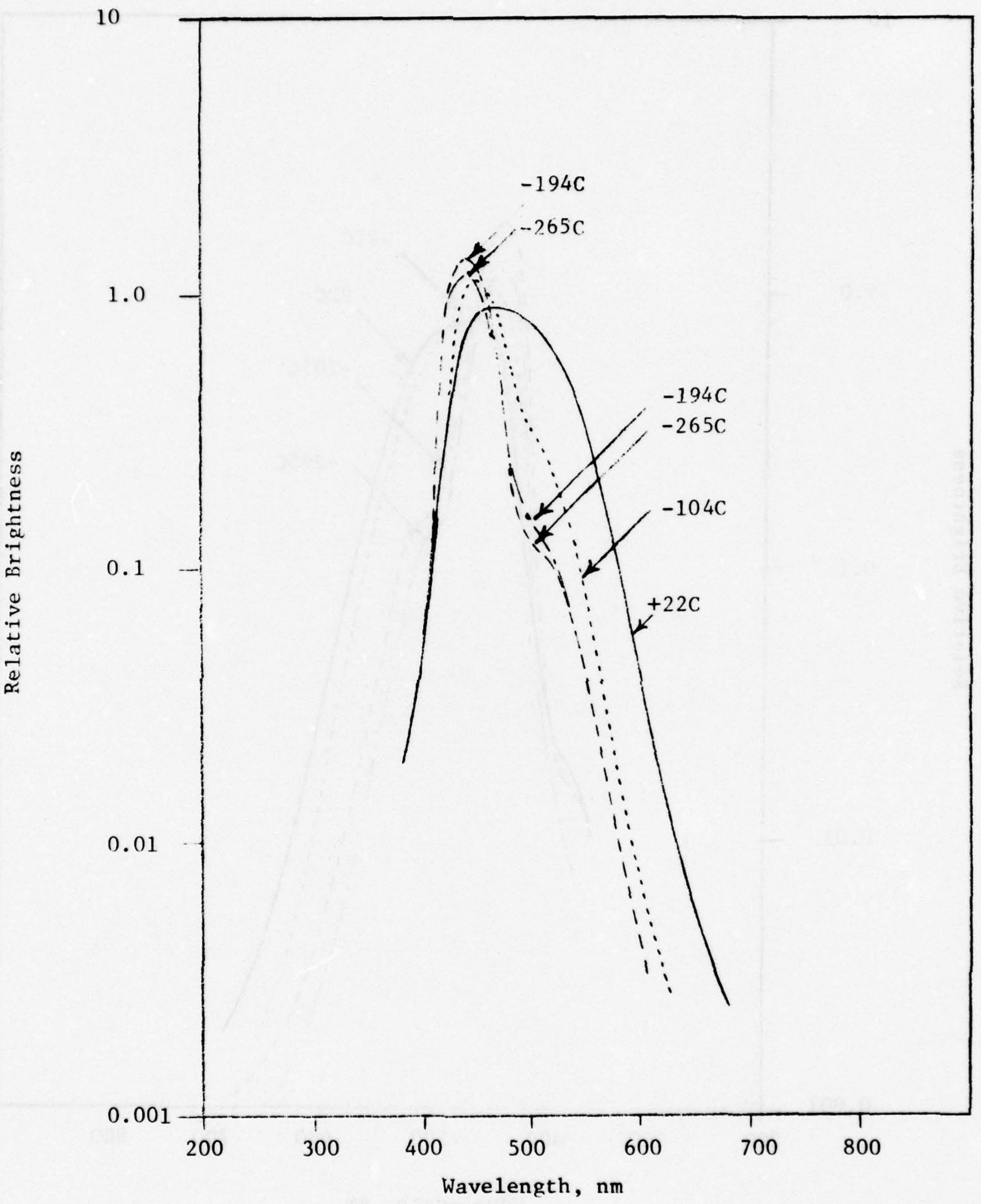

Figure 12. UV Excited Spectral Emission of Encapsulated Sylvania 723 Green Phosphor Lot 166-33B with 0.5-Micron Wall

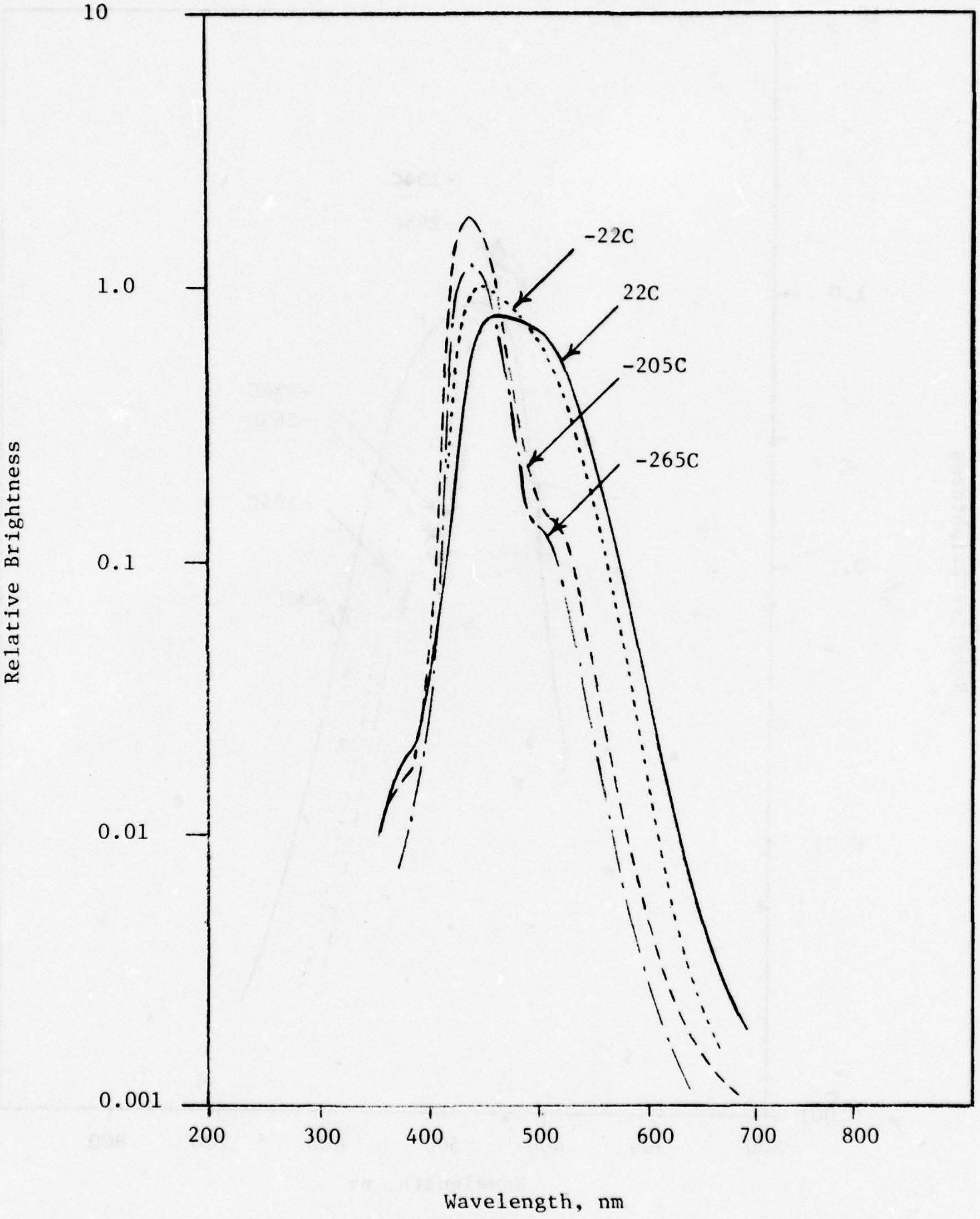

Figure 13. UV Excited Spectral Emission of Encapsulated Sylvania 723 Green Phosphor Lot 166-33B with 1-Micron Wall

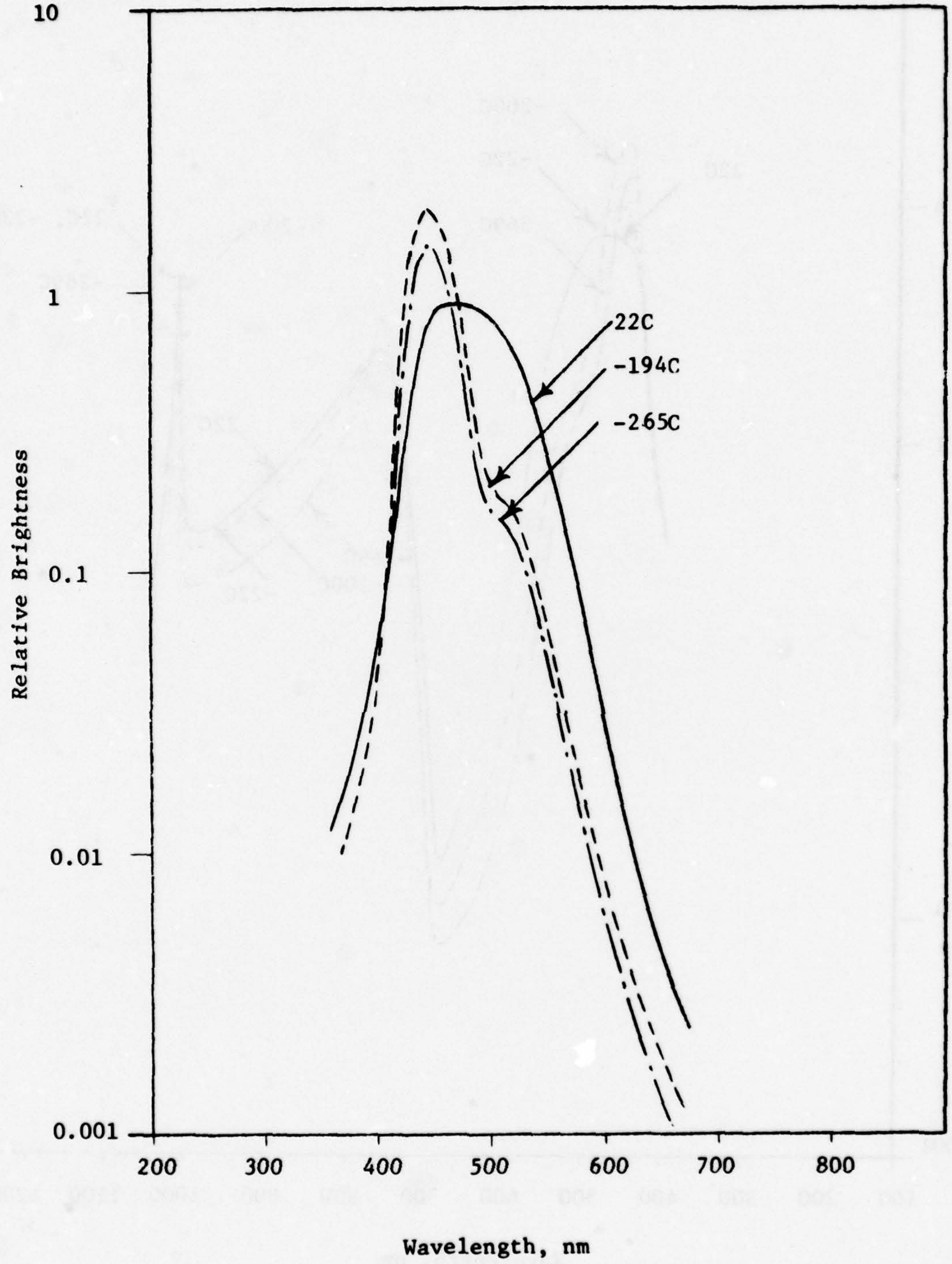

Figure 14. UV Excited Spectral Emission of Encapsulated Sylvania 723 Green Phosphor Lot 166-33B with 3-Micron Wall

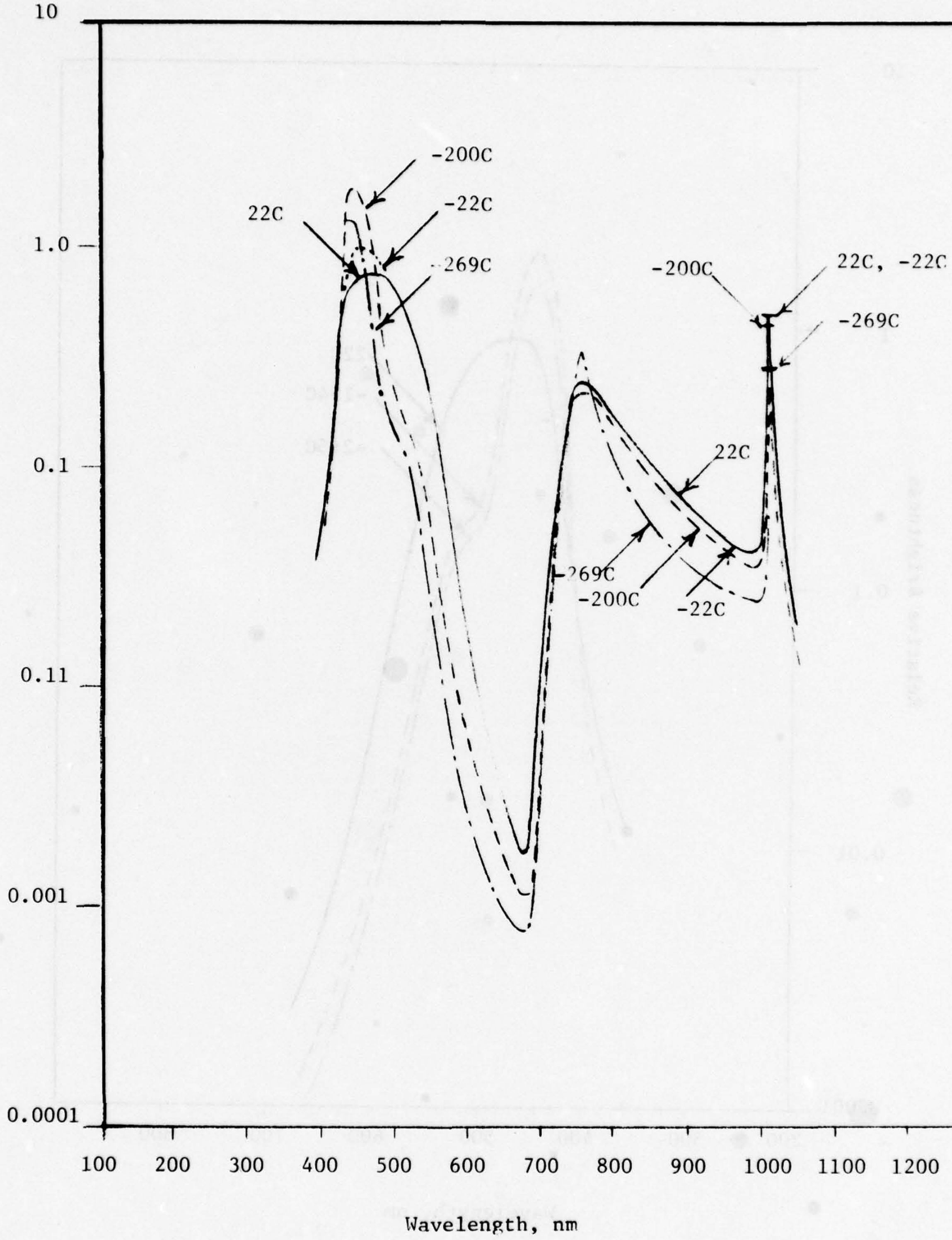

Figure 15. UV Excited Visible and Infrared Emission of Encapsulated Sylvania 723 Green Phosphor Lot 166-33B with 1-Micron Wall

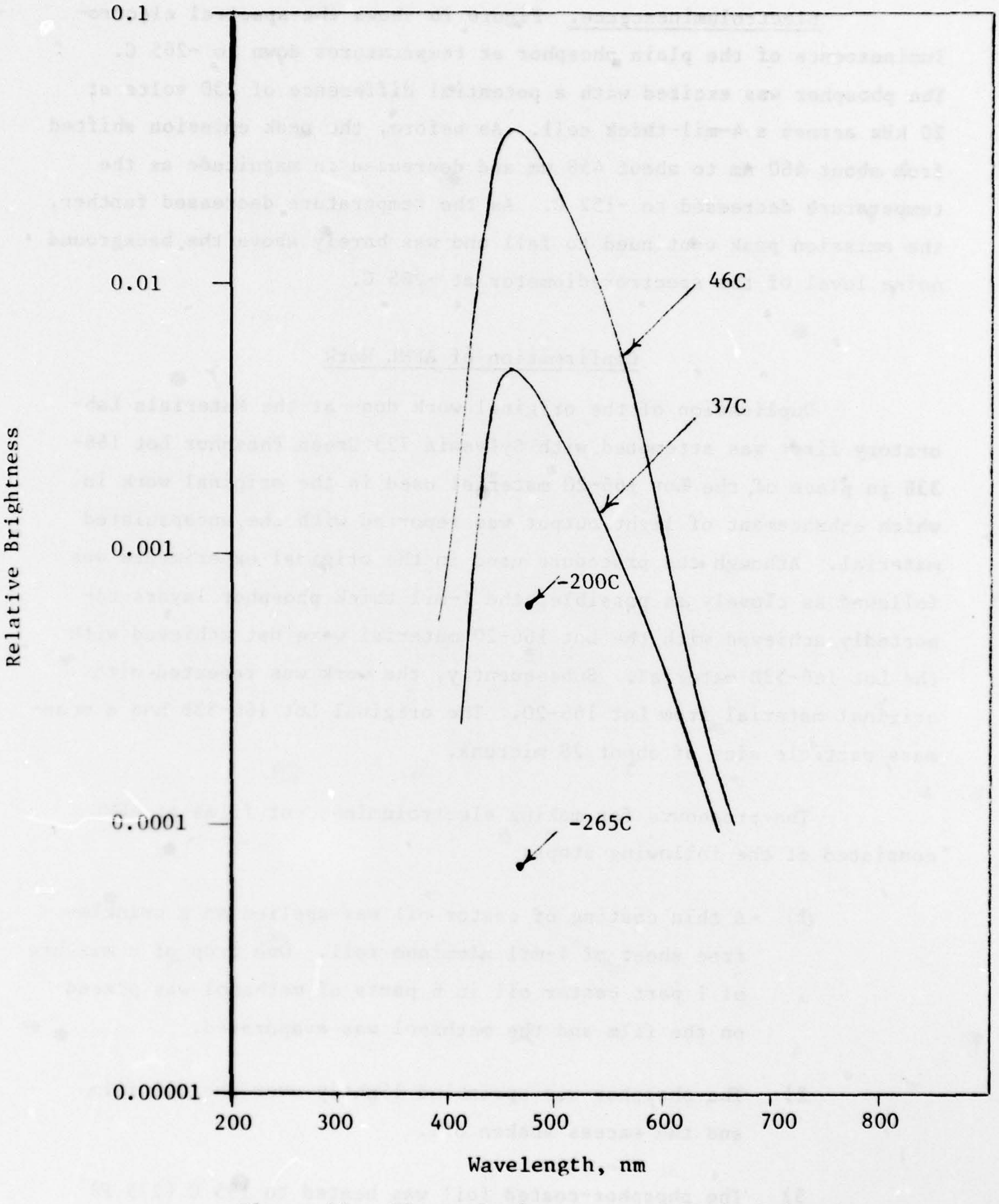

Figure 16. Electroluminescence of Plain Sylvania 723 Green Phosphor Lot 166-33B

Electroluminescence. Figure 16 shows the spectral electroluminescence of the plain phosphor at temperatures down to -265 C. The phosphor was excited with a potential difference of 230 volts at 20 kHz across a 4-mil-thick cell. As before, the peak emission shifted from about 460 nm to about 450 nm and decreased in magnitude as the temperature decreased to -152 C. As the temperature decreased further, the emission peak continued to fall and was barely above the background noise level of the spectroradiometer at -265 C.

Confirmation of AFML Work

Duplication of the original work done at the Materials Laboratory first was attempted with Sylvania 723 Green Phosphor Lot 166-33B in place of the Lot 166-20 material used in the original work in which enhancement of light output was reported with the encapsulated material. Athough the procedure used in the original experiments was followed as closely as possible, the 1-mil-thick phosphor layers reportedly achieved with the Lot 166-20 material were not achieved with the Lot 166-33B material. Subsequently, the work was repeated with original material from Lot 166-20. The original Lot 166-33B had a mean-mass particle size of about 28 microns.

The procedure for making electroluminescent films at AFML consisted of the following steps:

1) A thin coating of castor oil was applied on a wrinkle-free sheet of 1-mil aluminum foil. One drop of a mixture of 1 part castor oil in 6 parts of methanol was placed on the film and the methanol was evaporated.

2) The phosphor was sprinkled lightly over the oil film and the excess shaken off.

3) The phosphor-coated foil was heated to 135 C (275 F) and pressed between a pair of flat polished steel dies at 20,000 psi for 15 minutes while the temperature was maintained.

The resultant films were reported to be about 1-mil thick and were evaluated in a castor-oil-type test cell with a conductive Mylar window.

In the original AFML work, the films with unencapsulated phosphor of the same lot were prepared following the procedure except that the films were not heated or pressed.

Cells with Original Phosphor

Personnel from the Materials Laboratory assisted in resolving problems encountered in duplicating the original AFML work. Two differences in cell preparation were identified. The castor oil used in the Materials Laboratory was compatible with methanol while that used at Battelle was not. Also, in pressing films at the Materials Laboratory, the temperature of the film was held at 135 C (275 F) for 15 minutes, and the temperature was not held constant at Battelle.

Subsequently, a 1-mil film of encapsulated Sylvania 723 Green Phosphor Lot 166-20 was formed by heating to 135 C (275 F) and pressing for 15 minutes while cooling. Although the temperature was not held constant, the cell made with this film had a light output of about 4.5 ft L at 107 volts and 400 Hz, 17 ft L at 107 volts and 4 kHz, 21 ft L at 107 volts and 6 kHz, and 30 ft L at 107 volts and 14 kHz. The emission of the cell was comparable to that of several cells made at the Materials Laboratory which at 115 volts had average light output of 4.9 ft L at 400 Hz, 16 ft L at 4 kHz, 23.7 ft L at 6 kHz, and 35.7 ft L at 14 kHz. For comparison, a 1-mil cell made with plain phosphor of the same lot had light output of 6, 23, 25, and 37 ft L, respectively, at 107 volts and 400 Hz, 4 kHz, 6 kHz, and 14 kHz. In this comparison at 107 volts, the light output of the plain phosphor that was heated but not pressed was 20 to 30 percent higher than that of the encapsulated phosphor.

To reproduce the AFML work exactly, heating tapes were wrapped around the forming dies to maintain the temperature at 135 C (275 F); and, additional films were made with the same AFML materials and the original encapsulated Sylvania 723 Green Phosphor Lot 166-20 while the temperature was held at 135 C (275 F) for 15 minutes. The resultant films were all about 1.5 mils thick and were lighted in a test cell with either a Neda glass window or a window with metallized Mylar. Several films made by two different experimenters had light output of about 2.2 to 4.3, 9.2 to 15 and 12 to 19 ft L at 115 volts and frequencies of 400 Hz, 6 kHz, and 14 KHz, respectively. Reducing the pressing time from 15 minutes to 30 seconds produced cells with similar light output. For comparison, a cell made with plain phosphor of the same lot had light output of 6.8, 26, and 34 ft L at the same respective tests conditions. In these tests, the light output from the cells made with the encapsulated phosphor generally was significantly less than the light output from the cells made with the plain phosphor when prepared under identical conditions of heating and pressing. Shorter heating periods of about 30 seconds did not change the light output of the film.

The fact that the films made with plain phosphor at the AFML earlier were neither heated or pressed is believed to be a significant factor. Unprotected phosphor will pick up moisture which adversely affects the electroluminescent output. Heating drives off the moisture and essentially restores the light output to its original level.

Cells With CNEC Encapsulated Phosphor

A sample of Sylvania 723 Green Phosphor Lot 166-33B encapsulated with CNEC at the AFML was supplied in a water dispersion. The sample first was washed with distilled water and dried. The material as received contained some relatively large chunks of a black contaminant that largely were removed by filtering through a 325-mesh sieve. The encapsulated phosphor then was dried at 105 C and sieved again to break up agglomerates. Under magnification at 500X, the size and shape of the encapsulated particles appeared about the same as in the original phosphor.

Subsequently, the CNEC encapsulated phosphor was evaluated in a test cell using the AFML procedure for forming a 1.5-mil film. A 6.3-mm (1/4 inch)-diameter area of the film was tested in a cell with a Nesa glass window.

When pressed at 135 C (275 F) for 15 minutes, the CNEC turned dark yellow. Although the cells initially were bright, the light output decreased rapidly. Also the cells often shorted out at 115 volts as the frequency was increased from 400 Hz to 14 kHz. Better light output and stability were achieved in cells that were heated for only about 30 seconds at 275 F. Light output of about 17 ft L was measured at 115 volts and 14 kHz. Higher voltages and frequencies were not tested.

SECTION IV

THEORETICAL STUDY

The diametrical protuberances on the encapsulated phosphors represent a significant physical change in the matrix around the phosphor particles. Thus, theoretical studies were directed toward a review of optical theory to explain how the protuberances might affect the light output from a particle. The evaluation was based on the assumption that the protuberances might act as light tubes that collect and focus the emission from individual particles, that the protuberances might be oriented such that the light from the particles is directed in a given direction, and that the tubes might provide an effective system for delivering light from particles located below the surface layer of particles in a film.

The reflection phenomena at the phosphor-encapsulating coating interface and at the encapsulating coating-matrix interface were examined in detail.

Propagation of Radiation from ZnS into Encapsulating Coating

The light emitted by the phosphor particles first must pass from the particle into the surrounding wall such as shown in Figure 17. The phosphor particle has a refractive index μ_p, and the wall material has a refractive index μ_w. A ray of light emitted at point 0 in the phosphor strikes the interface at an angle θ_p from the normal to the interface, is bent, and emerges in the wall material at an angle θ_w from the normal to the interface.

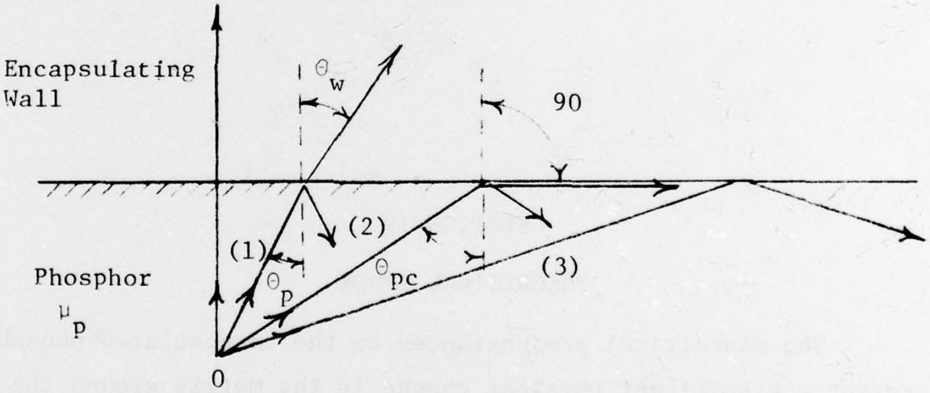

Figure 17. Light Beam at Interface of Phosphor and Wall

The refraction that occurs in the wall material is determined by the refractive indices of the materials, and the refraction angel, Θ_w, depends on the angle of incidence, Θ_p, as follows:

$$\frac{\sin \Theta_p}{\sin \Theta_w} = \frac{\mu_w}{\mu_p}$$

The refractive index of ZnS is about 2.4(1) and the refractive index of organic polymers such as used in the encapsulating walls is about 1.6(2). Thus, rays of light from the phosphor pass from a region of higher refractive index to a region of lower refractive index. Rays such as (1) passing through the interface are refracted at angles that are larger than the angle of incidence. Part of the light may be reflected at low angles, but as the angle of incidence increases, an angle is reached at which the rays such as (2) are totally reflected at the interface. This occurs when $\Theta_w = 90$ degrees. The critical angle of incidence Θ_{pc} at which total reflection occurs in the phosphor is:

$$\Theta_{pc} = \sin^{-1} \frac{\mu_w}{\mu_p}$$

Using the values of $\mu_w = 1.6$ and $\mu_p = 2.4$, the critical angle of total reflection at the interface between the phosphor and the wall material is about 42 degrees. Any rays such as (3) that strike the wall at angles greater than 42 degrees will be totally reflected.

Since emission originates at a variety of places in the phosphor and radiates into 4 π steradians, some radiation will escape at the first point of incidence and some only after multiple reflections, if at all. Thus, the radiation intensity from a ZnS particle encapsulated with a materials of refractive index lower than that of ZnS will never be larger than that from an equivalent unencapsulated particle and may be less due to absorption of internal reflections unless some further event occurs.

On the other hand if the refractive index of the wall material is larger than the refractive index of the phosphor, total internal reflection in the particle will not occur at any angle of incidence. Some reflection will always occur at the particle-coating interface; however, and the total emission still will not exceed that from an unencapsulated particle.

The light output due to internal reflection might be enhanced if the electroluminescence radiation included UV radiation. Internal reflection of such radiation might produce additional light by exciting photoluminescence in the phosphor, thereby increasing the overall light output. However, this effect would occur in any matrix which had a refractive index such that internal reflection occurred in the phosphor particles and it would not be unique in encapsulated particles.

Radiation in Wall Protuberances

Once the radiation enters the encapsulating wall, the shape of the wall and the refractive index of the medium outside the wall become determinants. Figure 18 is a sketch of an encapsulated phosphor particle with the diametric conical protuberances that were observed and photographed in the microexamination of the phosphor particles. Figure 19 is a simplified diagram of the conical protuberance showing the path of a light ray entering the base of the cone and emerging at the blunt end toward the apex end of the cone.

The path of the light rays depend on the refractive index, μ_w, of the encapsulating wall material making up the cone, the refractive index μ_m of the matrix outside the capsule wall, and the angle of incidence, Θ, of the incoming beam as follows:

1) When μ_m is larger than μ_w, part of the beam will always escape the cone at the first point of incidence and at every point of incidence of the reflected portion thereafter.

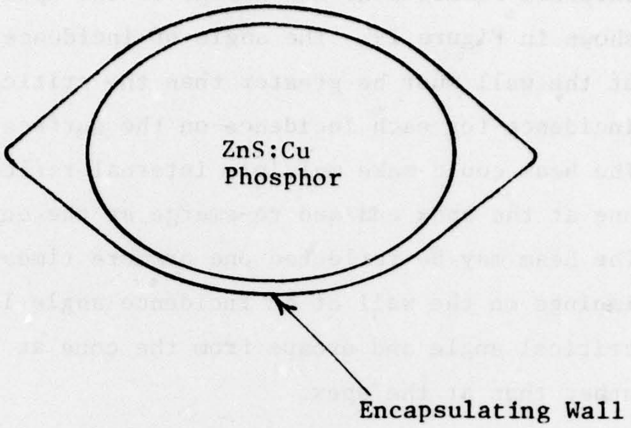

Figure 18. Encapsulated Phosphor Particle

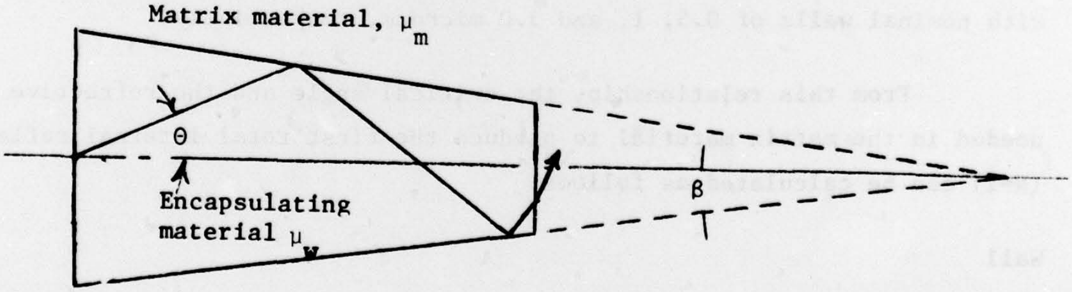

Figure 19. Propagation of Light Ray Through Conical Protuberance

2) When μ_m is smaller than μ_w, the beam may undergo multiple internal reflections and emerge at the apex of the cone as shown in Figure 19. The angle of incidence of the beam at the wall must be greater than the critical angle of incidence for each incidence on the surface.

3) The beam could make multiple internal reflections including one at the apex end and re-emerge at the entrance end.

4) The beam may be reflected one or more times and then impinge on the wall at an incidence angle less than the critical angle and excape from the cone at some point other than at the apex.

Internal reflection in the cone is related to the entrance angle, Θ, at the base of the cone as follows:

$$\theta \leq \frac{\pi}{2} - \theta_c - (2N-1)\ \beta,$$

where $\Theta_c = \sin^{-1} \frac{\mu_m}{\mu w}$ and is the critical angle of reflection between the encapsulating wall material in the cone and the matrix surrounding it, N is the number of internal reflections, and β is the half angle of the cone. Half angles of about 45, 36, and 17 degrees were measured for the particles with nominal walls of 0.5, 1, and 3.0 microns, respectively.

From this relationship, the critical angle and the refractive index needed in the matrix material to produce the first total internal reflection (N=1) can be calculated as follows:

Wall Thickness, microns	β, degrees	Θ_c, degrees	μm
0.5	45	$\geq$ 45	$\leq$ 1.13
1.0	36	$\geq$ 54	$\leq$ 1.29
3.0	17	$\geq$ 73	$\leq$ 1.53

For the first reflection to occur with light entering along the axis of the cone ($\Theta = 0$), the refractive index of the matrix material outside the cone must be less than 1.13, 1.29, and 1.53, respectively, for cones associated with the nominal 0.5, 1.0 and 3.0-micron encapsulated particles. In the limit case where $\mu_m = 1$ (air), the maximum entrance angle Θ at which the first reflection will occur is limited as follow:

Wall Thickness, microns	β, degrees	Θ_c, degrees	Θ, degrees
0.5	45	38.6	6.3
1.0	36	38.6	15.4
3.0	17	38.6	34.2

Even for the first reflection to occur in the cone, severe restrictions are placed on the matrix material and on the entrance angle. Even when the matrix material is air, light rays must enter the base of the cone at relatively small angles no greater than about 6 to 34 degrees for reflection to occur in the three cases of interest. Thus, the conical protuberances can not be expected to focus much of the radiation from a phosphor particle.

This theory predicts that the encapsulated phosphors with 3.0-micron walls would be better light emitters than the phosphors with 1.0-micron walls. Experiments do not support this result with electrically excited phosphors. Although the emission per unit amount of phosphor with UV excitation did increase with wall thickness, the total light output did not increase with wall thickness.

Radiation in Other Parts of the Encapsulant

The encapsulant is present on the entire surface of the EL particles and in regions other than those where the conical protusions occur. If the refractive index of the encapsulating wall is less than that of the phosphor, some rays will be totally reflected internally for one or more impingements on the interface. In view of normal shape irregularities, this will be a completely random situation. Few, if any, rays are likely to be permanently trapped, and the nonconical parts of the encapsulating material are not likely to have a net effect on directionality of the radiation.

Other Factors

Any preferred directionality imparted by the conical protusions in the encapsulant which may result in an apparent increase in brightness from the layer requires a preferred orientation of the particles (or cones). Furthermore, the refractive index of the encapsulant must be higher than that of the matrix. Even then the geometries and incidence angles are restricted.

More important, the electric field in the phosphor and hence the brightness of the output will increase with materials of higher dielectric constant as the matrix. Thus, a matrix with a high dielectric constant is desirable to achieve high brightness.

On the other hand, if the encapsulant cones are to have a beneficial effect, the matrix must have a dielectric constant lower than that of the encapsulant. Since the matrix is likely to occupy a much larger volume of the space surrounding the phosphor particles than the volume of the encapsulant, conditions will be opposite to those deemed on the basis of electric field considerations.

SECTION V
CONCLUSIONS

As a result of this program, the following conclusions were reached:

1) Encapsulation of phosphor particles with polyurethane type coatings does not increase electroluminescent light output but does reduce the tendency of the particles to disintegrate under stress. The light output decreases with increasing wall thickness.

2) Encapsulation of phosphor particles with polyurethane increases the normalized photoluminescence produced by UV excitation.

3) The encapsulated powders produced by the microencapsulation process have protuberances of material that do not appear to have any functional value for EL systems and which introduce a relatively large amount of inert material in films made with the phosphors.

4) Encapsulation of the phosphors apparently does not change the elemental structure of the phosphor although a significant amount of Si is included in the wall. The Si may have a deleterious effect in absorbing, diffusing, or scattering part of emission from the phosphors.

5) The peak of the spectral emission from the phosphors shifts to a shorter wave length as the temperature drops with either UV or electrical excitation. The effect is essentially the same for plain and encapsulated powders.

6) On a theoretical basis, no mechanism is seen that would predict a significant enhancement of light output as a result of encapsulation with a thin wall that might not also apply to any matrix material. The light-tube theory predicts that thick walls would produce more directionali-

zation of the emission from a phosphor particle than thin walls would produce. This is contrary to observed results with electrically excited phosphors.

7) Loss of light emission that may occur as a result of encapsulation appears to be largely due to electrical effects rather than to absorption of the light by the wall material in the materials studied.

* *

Data for this report are recorded in Battelle Laboratory Record Book 34178, page 1 to 75, inclusively.

APPENDIX 1

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APPENDIX II

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