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LASER-INDUCED FLUORESCENCE OF PHOSPHORS FOR REMOTE CRYOGENIC THERMOMETRY

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CONTENTS

LIST OF FIGURES

ABSTRACT

Remote cryogenic temperature measurements can be made by inducing fluorescence in phosphors with temperature-dependent emissions and measuring the emission lifetimes. The thermographic phosphor technique can be used for making precision, noncontact, cryogenic-temperature measurements in electrically hostile environments, such as high dc electric or magnetic fields. The National Aeronautics and Space Administration is interested in using these thermographic phosphors for mapping hot spots on cryogenic tank walls. Europium-doped lanthanum oxysulfide ($La_2O_2S:Eu$) and magnesium fluorogermanate doped with manganese ($Mg_4(F)GeO_6:Mn$) are suitable for low-temperature surface thermometry. Several emission lines, excited by a 337-nm ultraviolet laser, provide fluorescence lifetimes having logarithmic dependence with temperature from 4 K to above 125 K. A calibration curve for both $La_2O_2S:Eu$ and $Mg_4(F)GeO_6:Mn$ is presented, as well as emission spectra taken at room temperature and 11 K.

INTRODUCTION

The Oak Ridge National Laboratory (ORNL), in support of the National Aeronautics and Space Administration (NASA) Marshall Space Flight Center, Cryogenic Fluids Technology Office, performed laboratory investigations of a thermal-measurement concept using thermographic phosphors to remotely measure surface temperatures of 4 to 80 K. NASA is interested in developing thermal-measurement concepts that would be applicable for mapping hot spots on cryogenic fuel tank walls and determining the thermal stratification in a low-gravity cryogenic fluid. In handling and storing cryogenic fluids, the occurrence of hot spots on the container wall is of importance because of increased boil-off and the effect on fluid transfer. Determining the size, location, and distribution of such hot spots is vital to determining courses of action, such as design changes, to mitigate or eliminate the hot spots. ORNL previously performed low-temperature-calibration studies which showed that lanthanum oxysulfide doped with europium (La_2O_2S:Eu) could be used to measure temperature from liquid nitrogen ($-194°C$) to room temperature.[1] This paper describes investigation on the feasibility of using lanthanum oxysulfide doped with europium, lanthanum oxysulfide doped with terbium (La_2O_2S:Tb), or magnesium fluorogermanate doped with manganese (Mg_4(F)GeO_6:Mn) for temperature measurements of 4 to 80 K. Temperature calibration curves for La_2O_2S:Eu and Mg_4(F)GeO_6:Mn will be presented. Several binders are evaluated for adhering the phosphors to stainless-steel surfaces, and these results are also presented.

THERMOGRAPHY PHOSPHORS CONSIDERED FOR CRYOGENIC MEASUREMENTS

Strong temperature dependence exists in both of the lanthanum oxysulfide phosphors because of the competition between nonradiative-lattice de-excitation processes and photon-emitting de-excitation within the europium or terbium electronic levels. Details of this interaction are described by Fonger and Struck.[2] From the studies by Fonger and Struck, as well as earlier Oak Ridge studies[1,2,3,4] of La_2O_2S:Eu, its temperature dependency from ~80 K to above 500 K is well documented. In Figs. 1 through 3, the room-temperature emission and excitation spectra for La_2O_2S:Eu, La_2O_2S:Tb, and Mg_4(F)GeO_6:MN are shown, respectively. Figures 4 through 6 show emission spectra for each of the three phosphors for a given cryogenic temperature.

In the initial screening process, both the La_2O_2S:Eu and Mg_4(F)GeO_6:Mn showed excellent potential in the temperature range of interest, while the La_2O_2S:Tb showed no evidence of temperature dependence. With the La_2O_2S:Eu, the fluorescence lines of interest for the cryogenic temperatures were 418 and 446 nm although we also monitored the 514-, 538-, and 624-nm lines. When looking at the Mg_4(F)GeO_6:Mn, the 657-nm lines showed excellent cryogenic temperature dependence. The 623- and 638-nm lines were also monitored. In looking at the La_2O_2S:Tb, it was hoped that a cryogenic temperature-dependent line in the 460 to 500-nm range could be found. A cursory look at the La_2O_2S:Tb indicated little or no temperature dependency over the range of interest.

Measurements with La_2O_2S:Eu near room temperature have exhibited temperature dependencies allow determinations with <0.5°C uncertainty.[4] In these initial feasibility studies, determining if phosphor thermography could be used to measure cryogenic temperatures in the region of 4 to 80 K was the issue rather than accuracy. Thus, the main objective of this report is to present data that have been collected on La_2O_2S:Eu and $Mg_4(F)GeO_6$:Mn at temperatures ranging from 4 to 80 K.

DESCRIPTION OF THE THERMOGRAPHIC CRYOSTAT

The design objective was to provide a variable-temperature cryostat that could be used to investigate various phosphors' responses to cryogenic temperatures from liquid nitrogen (LN) down to liquid helium (LHe) temperatures. Such an apparatus was designed and fabricated and will be described in the following paragraphs.

The cryostat shown in Figs. 7 and 8 was designed to fit an existing research Dewar. Figure 9 gives a detailed cross-sectional view of the thermographic phosphor sample holder. The phosphor was placed in a 0.64-cm-diam cup in the end of a copper spindle. A heater was wrapped around the spindle just below the phosphor cup. A thermocouple (Au-0.07% Fe vs chromel) junction was mounted just below the cup to provide for temperature measurements. The reference junction for this thermocouple was immersed in the LHe bath at 4.16 K. Thus, the temperature differentials relative to the LHe bath temperature could be measured. Using standard thermocouple tables, an accuracy of better than 1 K could be obtained. A vishay cryogenic linear temperature sensor (CLTS) was also mounted on the copper spindle to allow additional absolute temperature measurements with a precision of ~2 K.

The copper spindle was sealed into a 0.64-cm Swagelok fitting that was welded into a long, 1.91-cm-diam, stainless-steel tube. Thus, the measurements could be carried out with either vacuum or helium vapor around the phosphor. Two optical fibers were mounted in the tube to bring in the 337-nm ultraviolet (UV) light from a nitrogen laser and transmit the emitted light back out to the monochrometer. The Swagelok fitting could be unscrewed to allow a new phosphor to be evaluated. A piece of 1.27-cm-diam thin-wall stainless-steel tubing extended from the spindle down into the LHe bath. A 25-turn-length of 0.1-cm-diam copper wire was wrapped around this tube to provide a heat leak from the bath to the spindle. The thermocouple, CLTS, and heater leads came through this tube and exited into the bath. The leads were hermetically sealed into the end of the copper spindle with Stycast 2850FT epoxy.

In operation, the phosphor tube and Dewar were evacuated and purged with helium gas. The Dewar was then filled with LHe to the desired level. If the temperature desired was at or near LHe temperature, the level was raised until the copper spindle was immersed. The temperature of the phosphor could be increased by elevating the spindle with respect to the LHe level or energizing the heater to provide fine temperature control. The temperature could be controlled within 0.1 K during a measurement sequence on the phosphor.

SETUP FOR CRYOGENIC TEMPERATURE MEASUREMENTS

A schematic of the screening and calibration setup is shown in Fig. 10. A pulsed-nitrogen laser (337-nm wavelength) was used to produce the excitation signal. The signal was carried from the laser via an optical fiber (600 μm diam, plastic-coated silica) to the sample that consisted of a thin packed film of the phosphor of interest. The phosphor was housed in the copper spindle cup described under in the previous section where the technique for controlling the temperature is also described. The cooling liquid was supplied by a 1000 L LHe storage Dewar to the cryogenic research Dewar.

The fluorescent emission signal was picked up by the same type of optical fiber mentioned previously and carried into a monochrometer where the wavelength was selected. The signal then entered the photomultiplier tube from which the amplified signal was displayed on a Tektronics 7854 waveform-analyzing oscilloscope. The fluorescent signals were then permanently stored on a computer via a GPIB interface. Fluorescent-emission spectral information was also obtained at different temperature levels by automatically varying the emission wavelength on the monochrometer and recording the output of the photomultiplier on a strip-chart recorder.

COLLECTING AND ANALYZING THE TEMPERATURE DATA

Several runs were made in each temperature range for the $La_2O_2S:Eu$, and each temperature datum was the average of four individual readings. This calibration study concentrated on a temperature range between 4 and 80 K, and several higher-temperature points were taken to verify concurrence with previously obtained data. The 446-nm-emission line representing the $^5D_3$ transition was examined, and a plot of the results of this investigation, as well as our earlier investigation, are shown in Fig. 11. The temperature, in Kelvin, is plotted against the log of the emission lifetime in microseconds.

Only two runs were completed with the $Mg_4(F)GeO_6:Mn$ prior to using the available LHe. Program limitation did not allow for the purchase, transfer and setup of addition LHe. The 657-nm emission line was examined over the range of 13 to 145 K. The data are plotted in Fig. 12 as the temperature in Kelvin vs the log of the emission lifetime in milliseconds. In the future, we hope to be able to perform a more extensive and detailed calibration study of the $Mg_4(F)GeO_6:Mn$.

BINDER EVALUATION

The binders' evaluation was an initial investigation for determining if available binders could be used to apply the phosphors to a 304 stainless-steel surface and survive the cryogenic environment. Three binders were chosen for the evaluation. Two of the binders were Stycast epoxy binders previously used in cryogenic service at ORNL (1266 and 1269A). The third binder chosen was a Sperex SP-115 binder that had been used in a wide variety of applications under temperature conditions ranging from room temperature to 1000°C.

Each of the three binders was used to apply La_2O_2S:Eu to two 304 stainless-steel coupons. The surface preparation consisted of sand blasting the coupon surface with 200-grit aluminum-oxide and then cleaning the surface with acetone. The binders were then mixed with the phosphor and applied to the coupons. A thin layer of the Stycast binder/phosphor mix was applied using a small spatula. The Sperex binder was applied using a commercial air brush. Figure 13 shows each of the binder/phosphor coupons excited by a UV light source.

Once the curing cycle was complete, a fluorescent emission spectra was run on each of the binder/phosphor coupons. The A coupons for each binder was cycled between liquid nitrogen and boiling water. The transient time for each cycle was 5 min in the LN and 5 min in the boiling water. This was repeated three times, and a second fluorescent spectra was run on each of the three coupons.

There was no evidence of deterioration, cracking, or peeling of any of the three binders. Furthermore, there was no change in the fluorescent spectra for any of the three coupons. These preliminary tests indicated that all of the binders tested could be used in cryogenic service for short-term use. For consideration for long-term service, additional testing would be required.

CONCLUSIONS

These initial feasibility studies indicate that both the La_2O_2S:Eu and $Mg_4(F)GeO_6$:Mn phosphors can be used to measure cryogenic temperatures over the range of 4 to 125 K. The three binders, Stycast 1269A and 1266 and the Sperex SP-115, all performed well in the initial screening tests. There was no evidence of deterioration, cracking, or peeling of any of the binder/phosphor mixes. The phosphor thermography technique appears to be an excellent candidate for the use in mapping hot spots for cryogenic fuel tanks. The next step in pursuing this concept is to define the required precision, as well as the service length required, of a thermographic phosphor system. Areas that might be considered for additional study are as follows:

1. Improvement of the measurement process with the existing laboratory arrangement to establish limits on precision for phosphors studied. This would include both optimizing the use of the instrumentation and analysis of the data.
2. Investigations of new phosphors for strong temperature response at cryogenic temperatures. Included would be theoretical considerations of phosphor fluorescence mechanism and calibration of candidate materials.
3. Innovations in the instrumentation. Multiple phosphor targets, improved temperature monitoring, shorter cool-down and heat-up cycles, more efficient use of LHe, optimizing the optical system, improvement of on-line analysis programs for better display, and direct data graphing and fit-smoothing routines would be considered.
4. Long-term service testing of candidate binders for space applications.
5. Incorporation of the thermographic phosphor system into a liquid hydrogen system at a NASA facility.

The thermographic phosphor technique could also be used for other cryogenic applications such as:

1. Measuring the surface temperatures of an operating LOX bearing. This would better define the true operating parameters and potentially lead to design changes that could extend bearing life considerably.
2. Monitoring the temperature of operating test articles inside NASA's Space Environmental Chambers.
3. Performing precision, noncontact cryogenic temperature measurements in electrically hostile environments such as high dc electric or magnetic fields.

ACKNOWLEDGMENTS
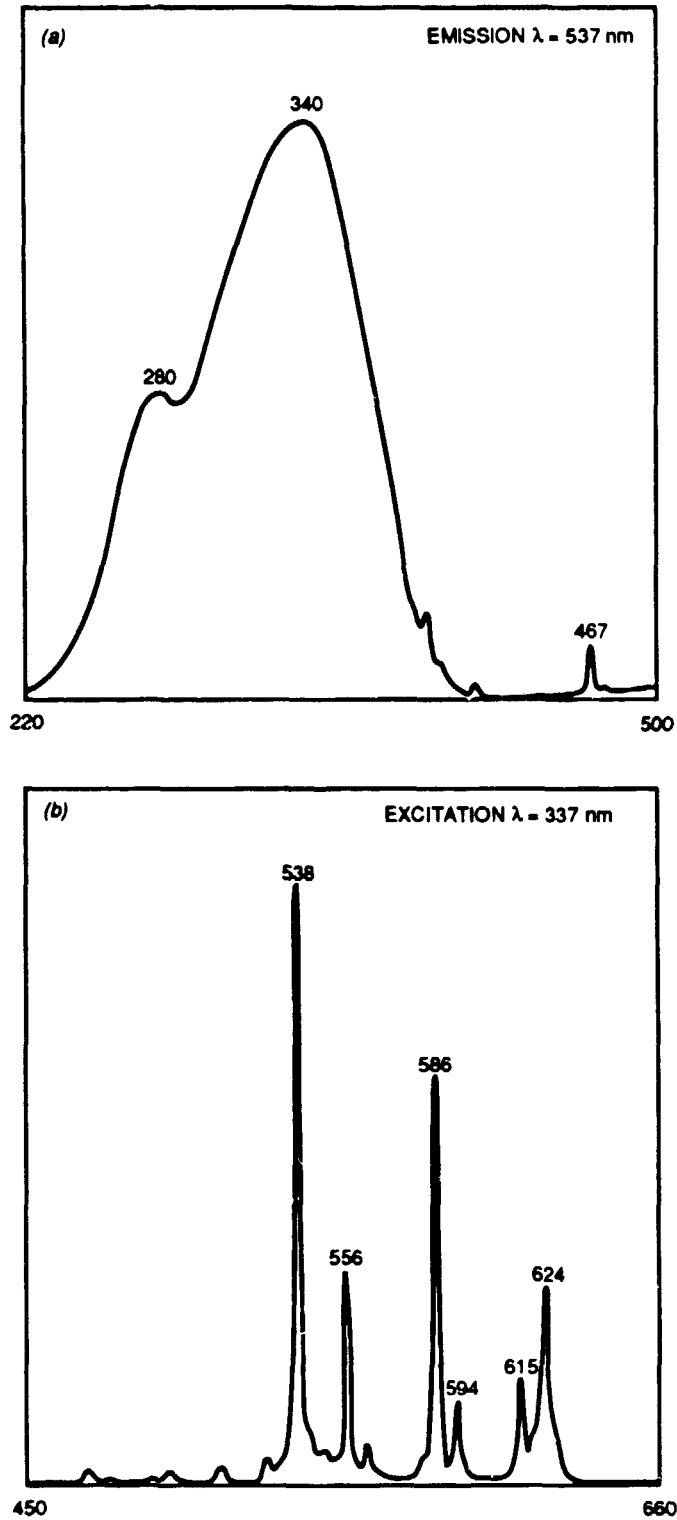
Fig. 1. Fluorescent excitation and emission spectra for La$_2$O$_2$S:Eu at room temperature. (a) excitation spectra, (b) emission spectra.
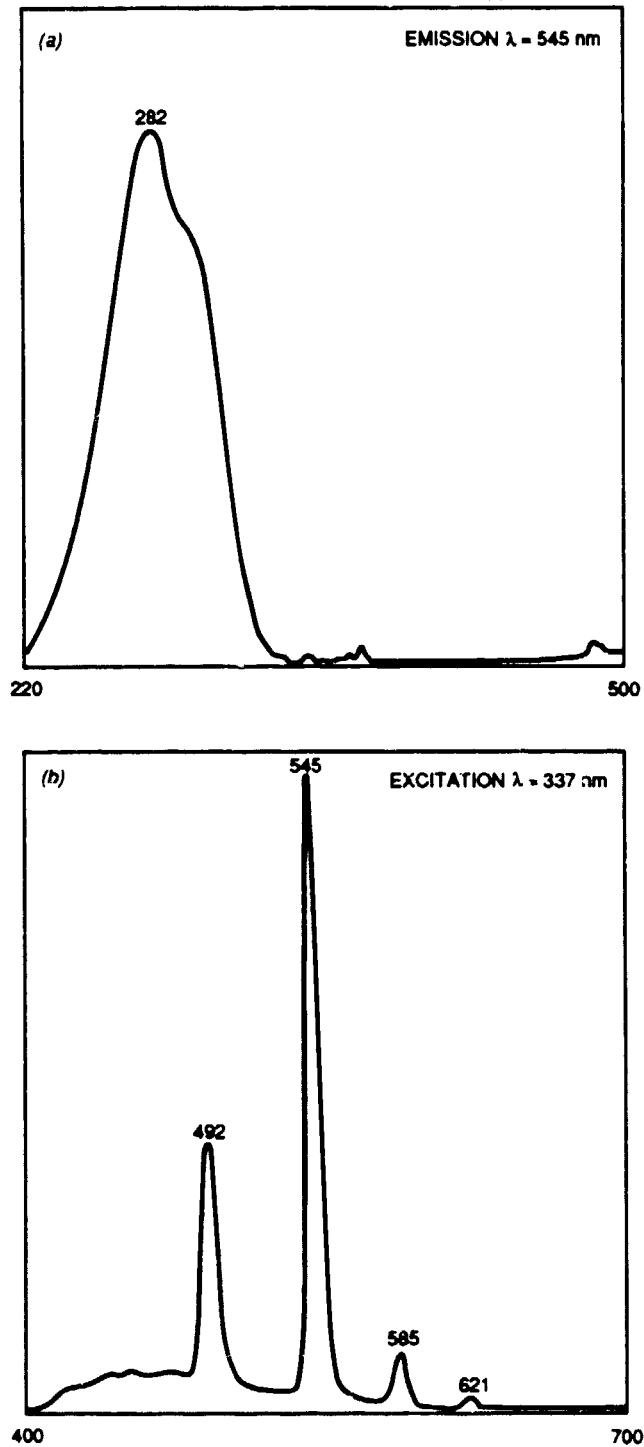
Fig. 2. Fluorescent excitation and emission spectra for La_2O_2S:Tb at room temperature. (a) excitation spectra, (b) emission spectra.
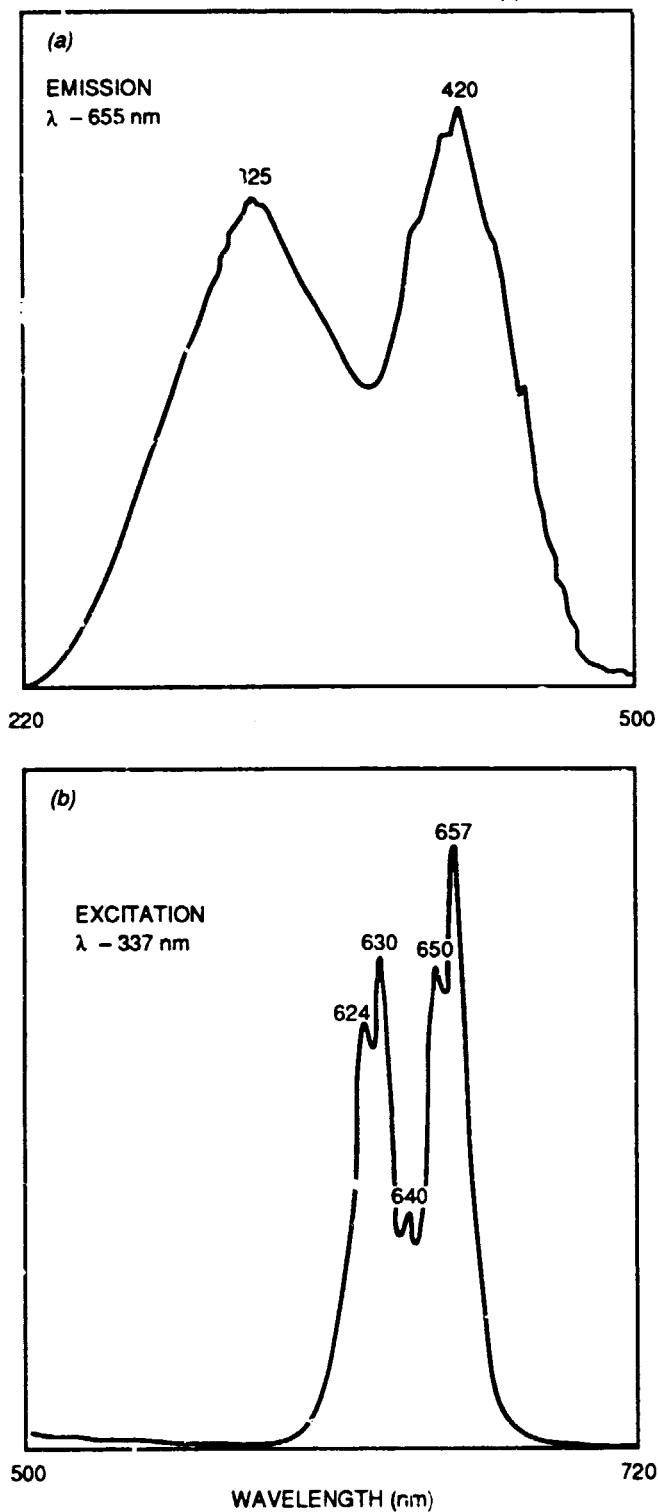
Fig. 3. Fluorescent excitation and emission spectra for
$Mg_4(F)GmO_6$:Mn at room temperature. *(a)* excitation
spectra, *(b)* emission spectra.
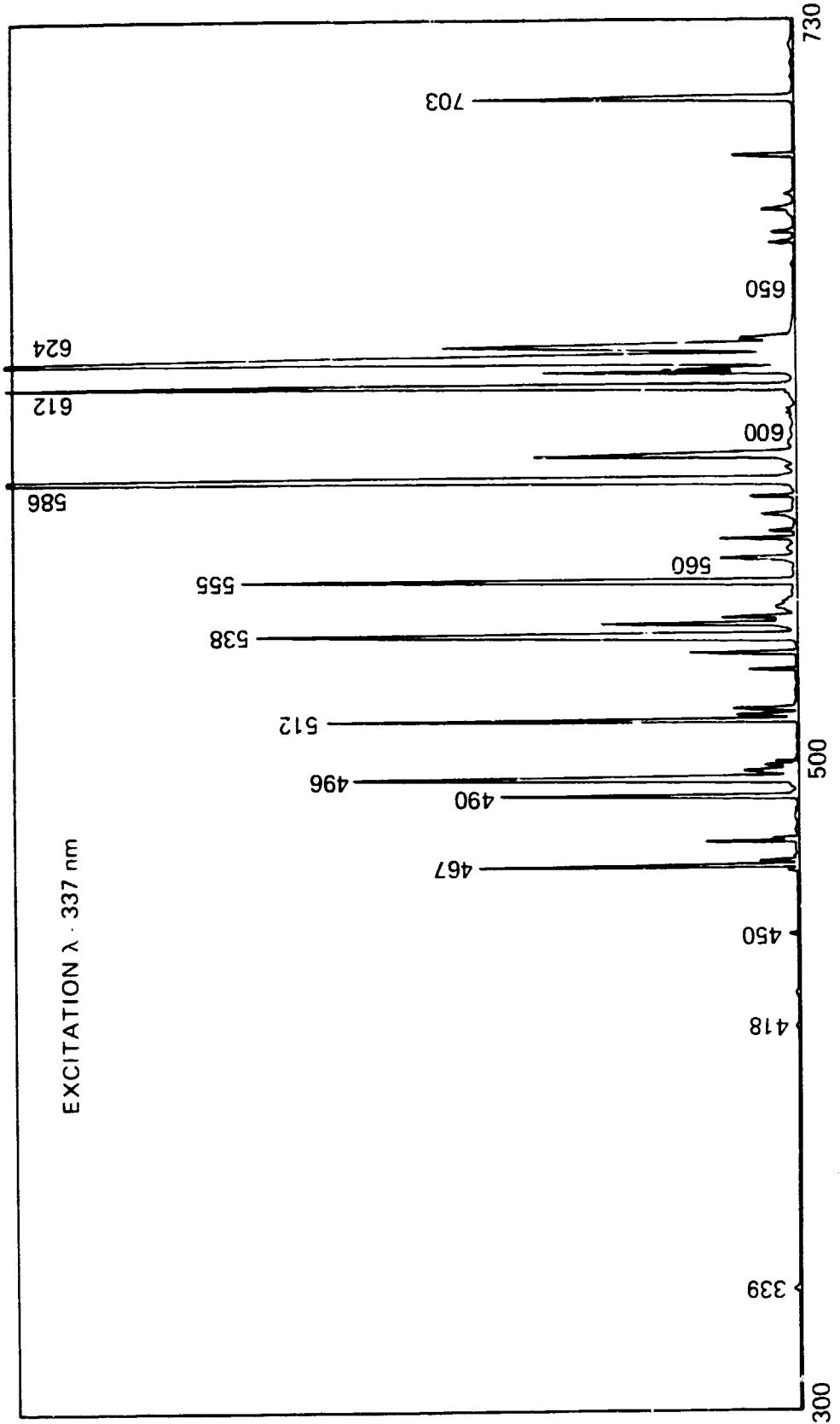
Fig. 4. Fluorescent emission spectra for La$_2$O$_2$S:Eu at 11K.

11
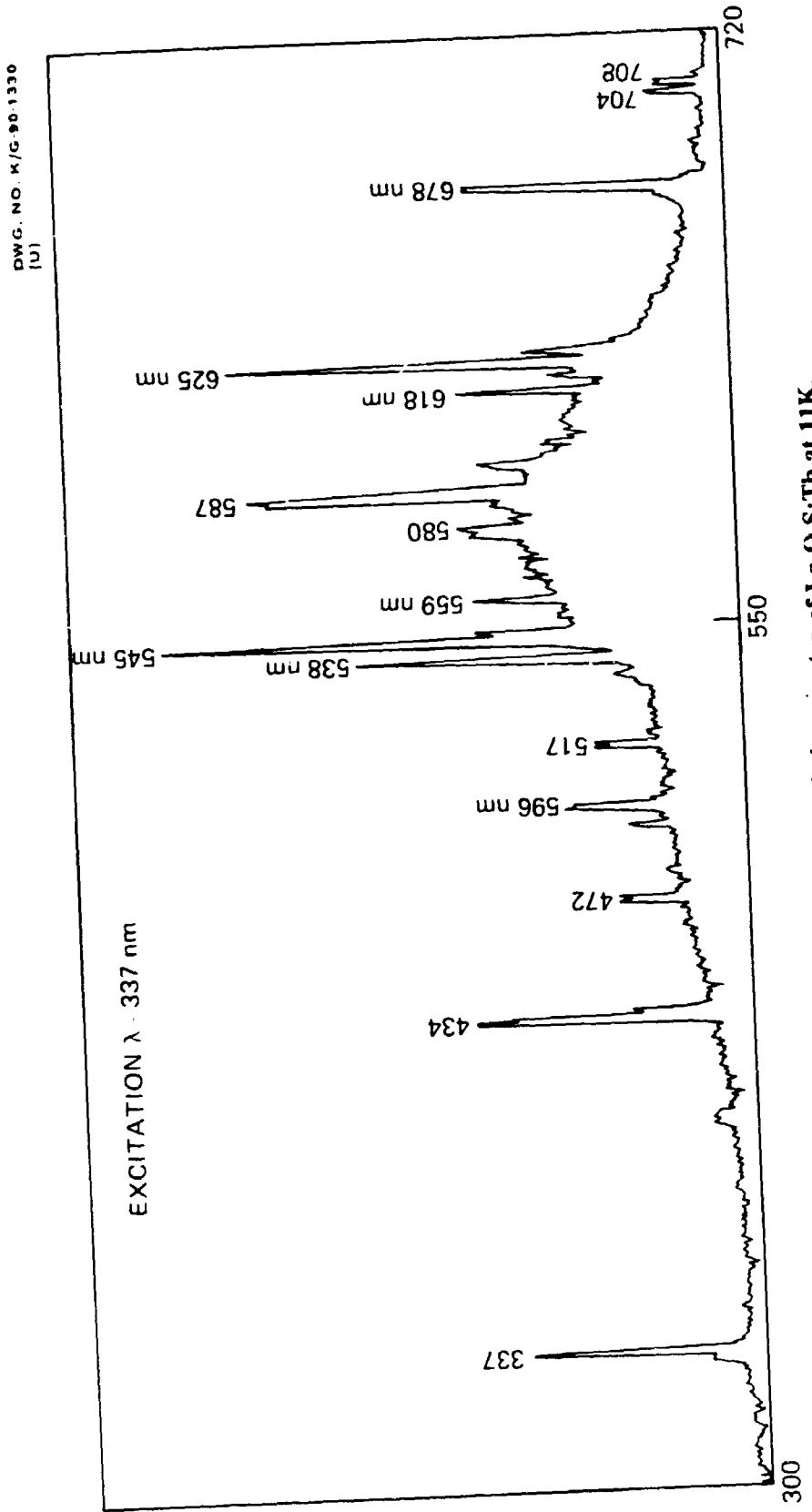
Fig. 5. Fluorescent-emission spectra of La_2O_2S:Tb at 11K.
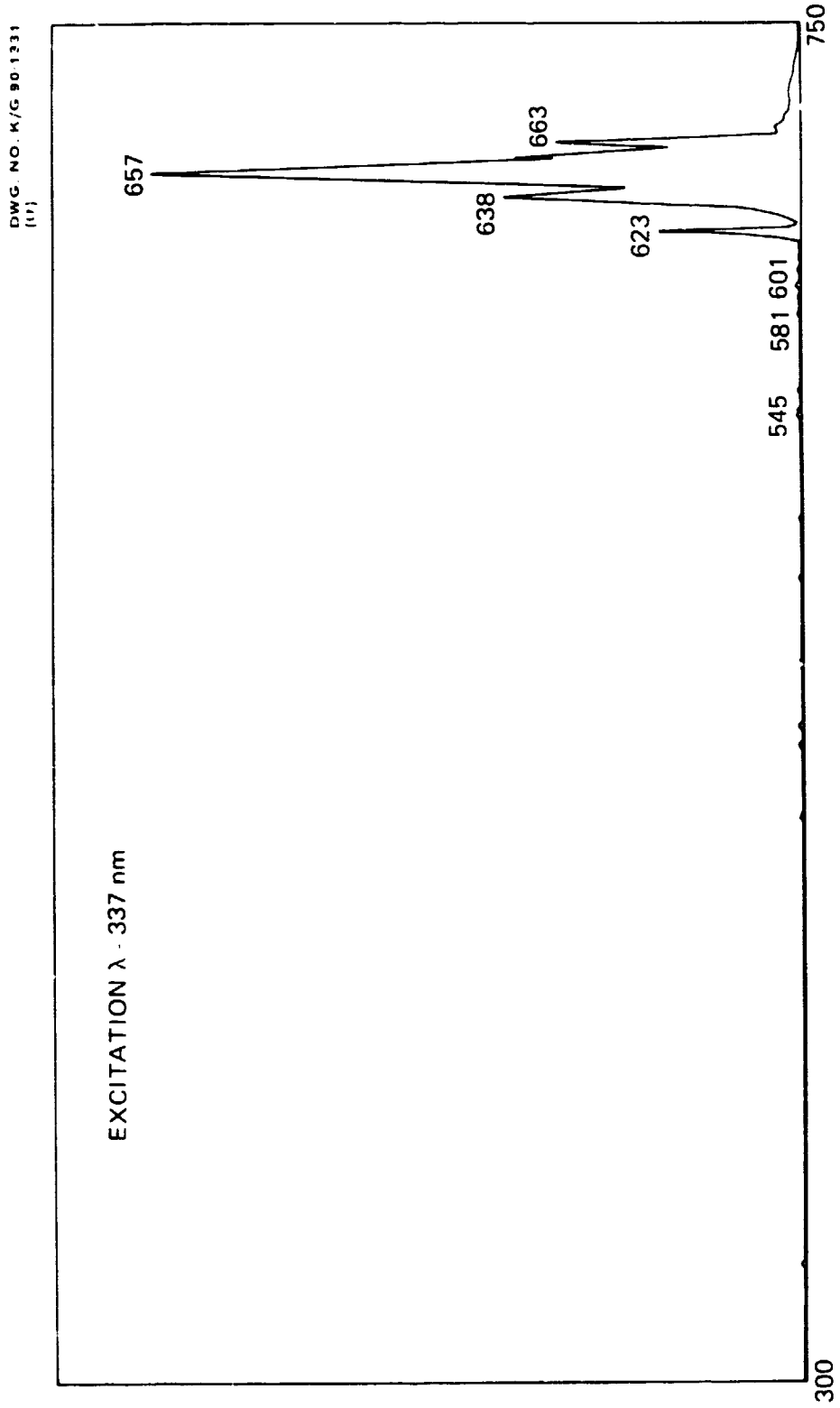
Fig. 6. Fluorescent emission spectra of $Mg_4(F)GmO_6$:Mn at 12K.
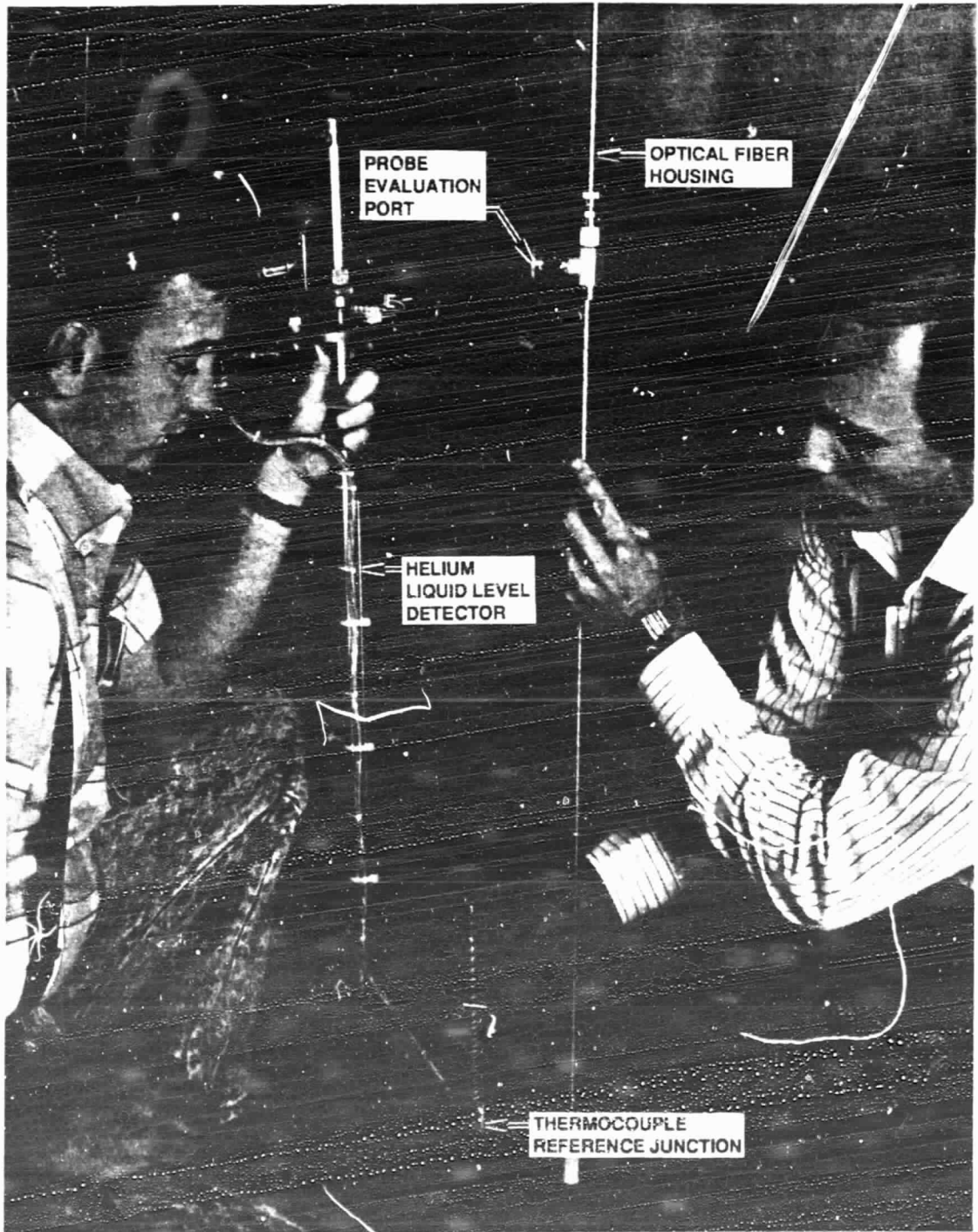
Fig. 7. Cryostat for thermographic phosphor experiments.
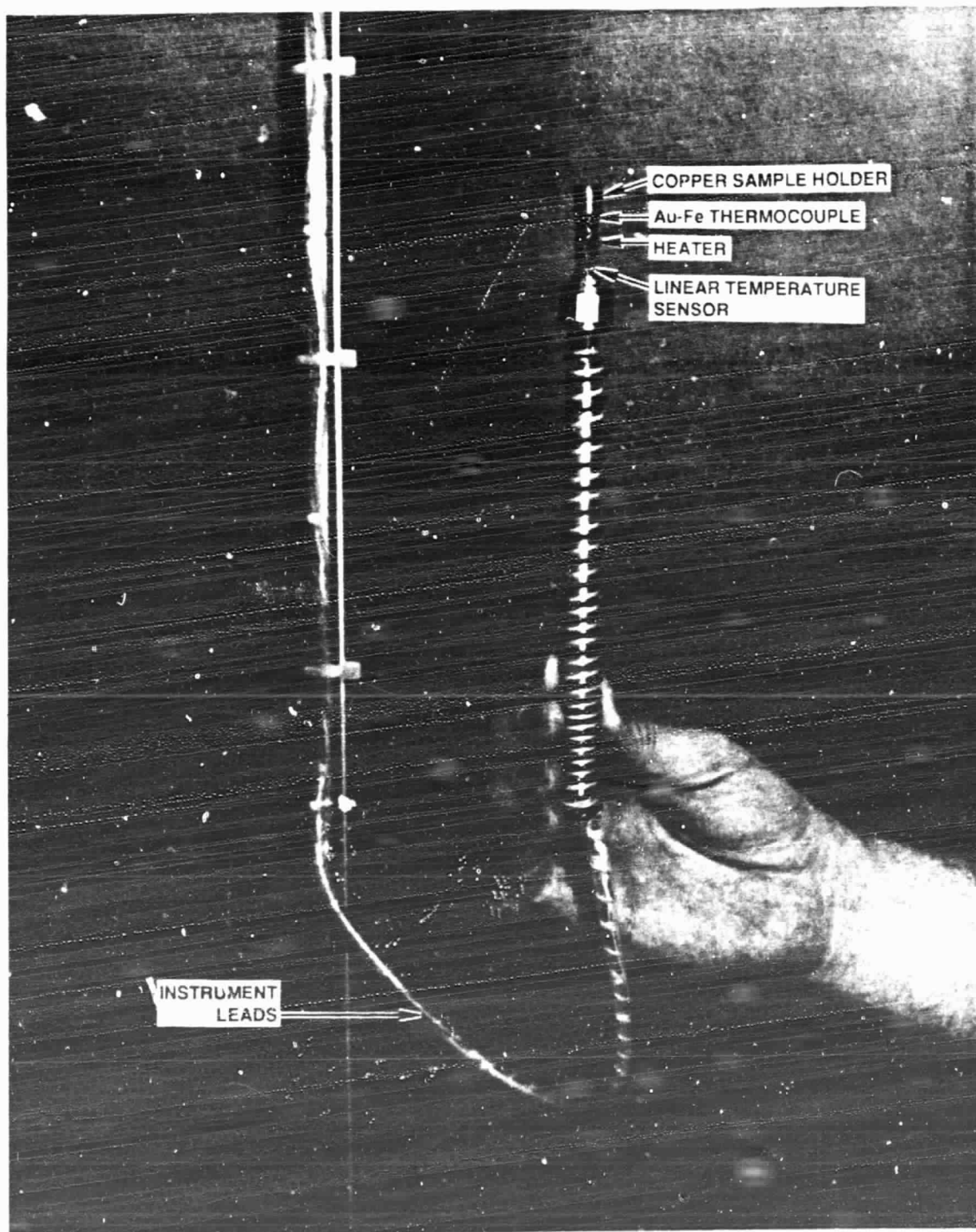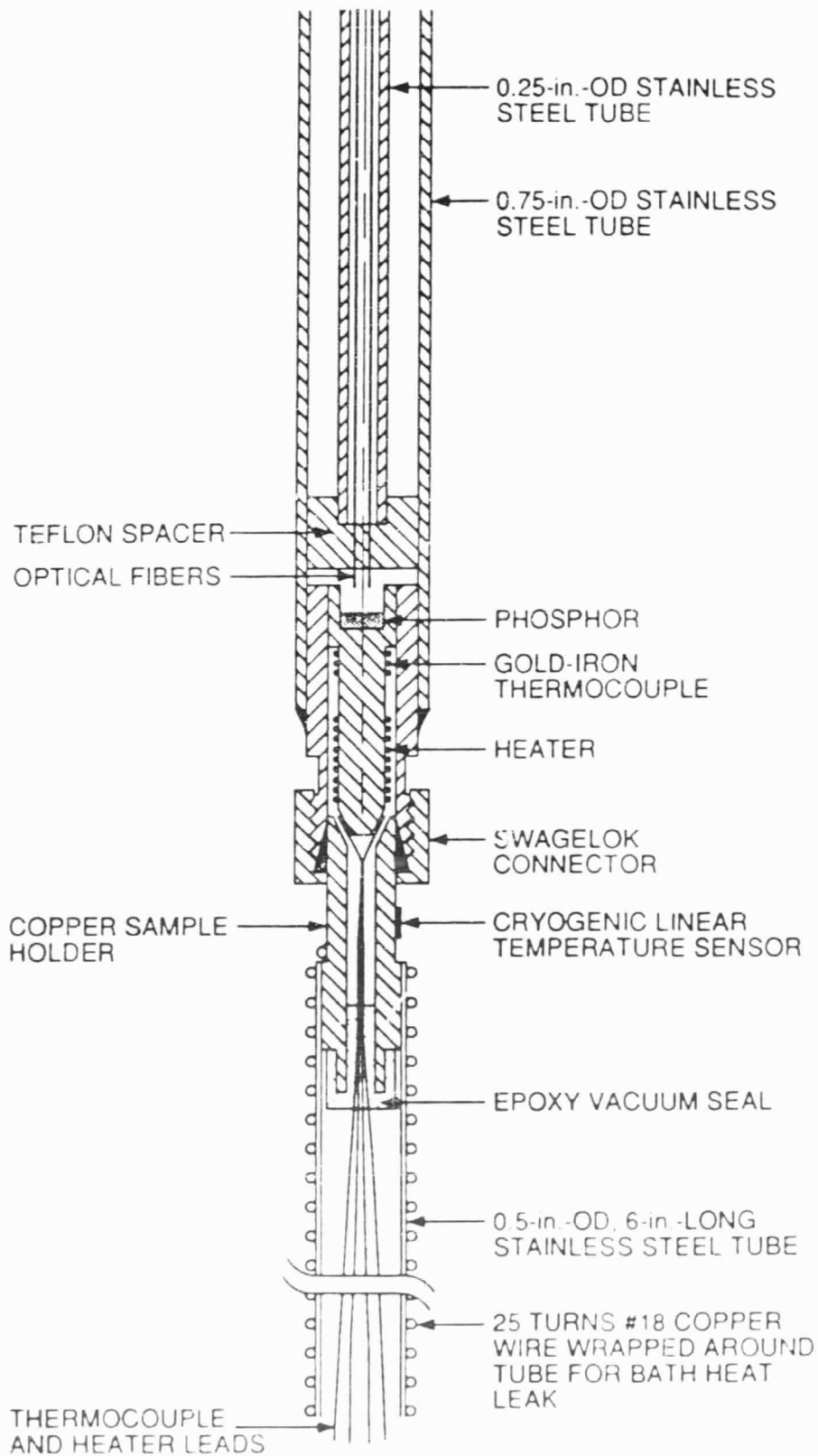
Fig. 8. Photograph of the crystat sample holder.

15

ORNL-DWG 90M-2452 FED

Fig. 9. Thermography sample holder.
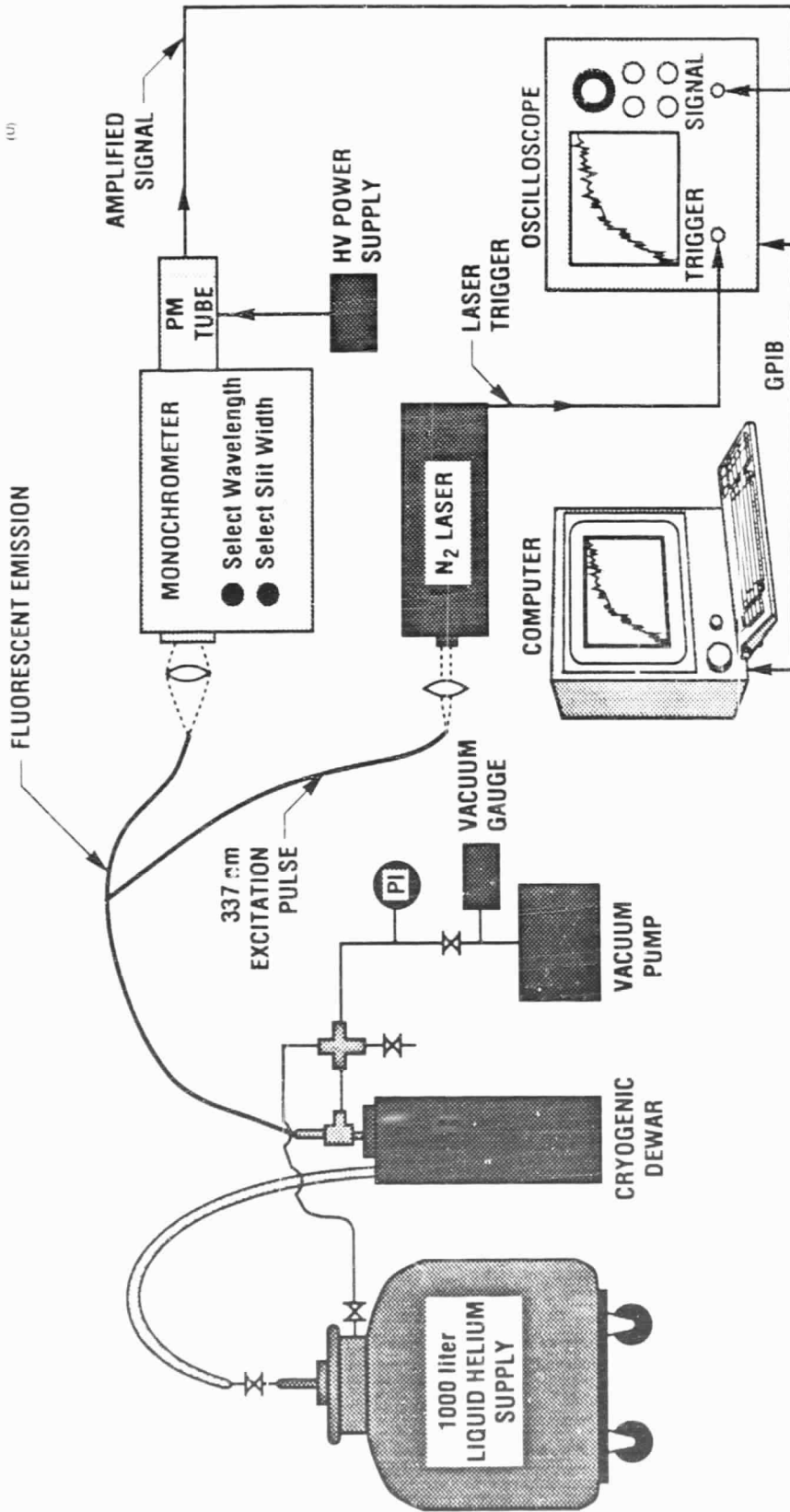
Fig. 10. Cryogenic temperature calibration setup.
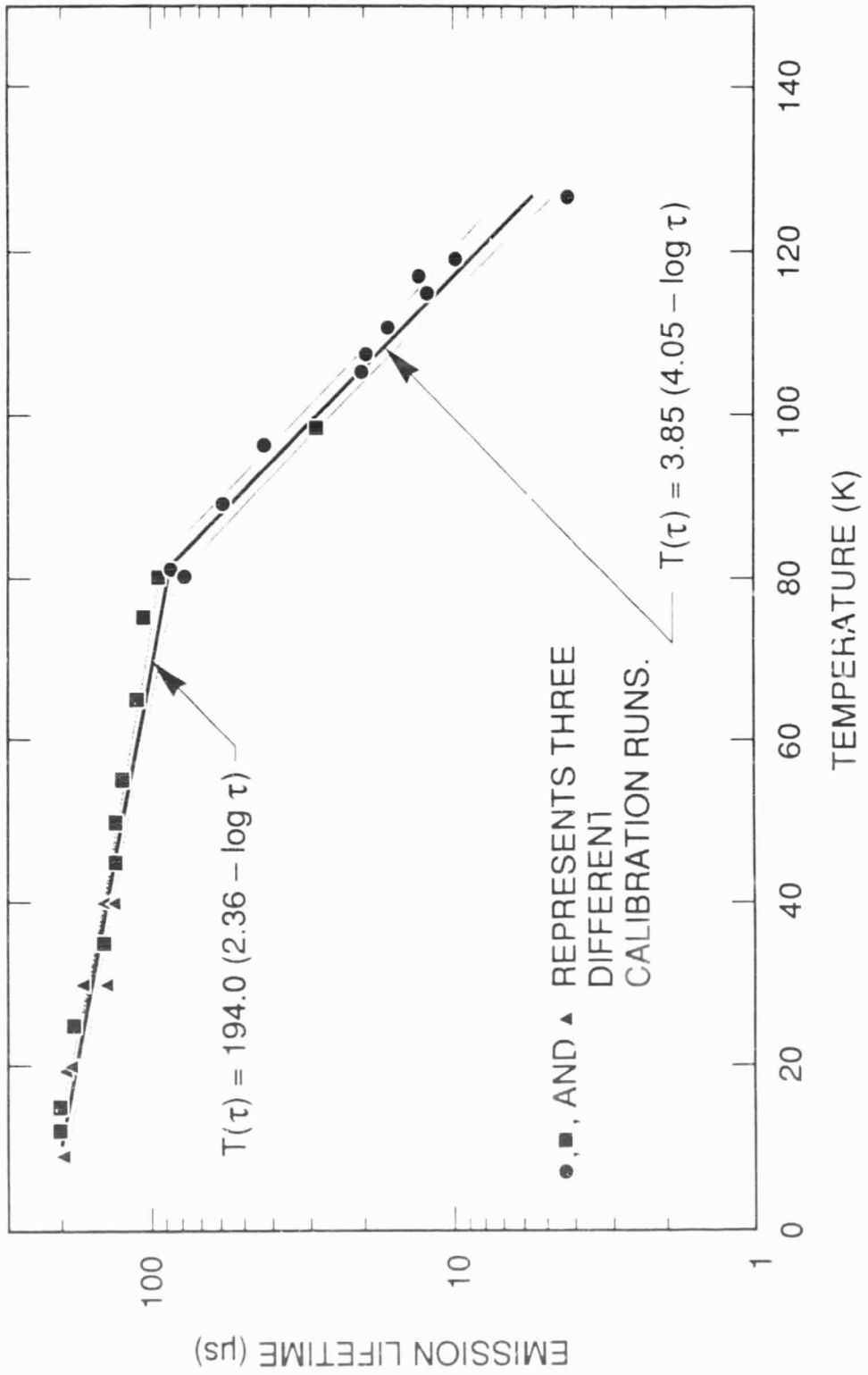
Fig. 11. La$_2$O$_2$S:Eu phosphor calibration.
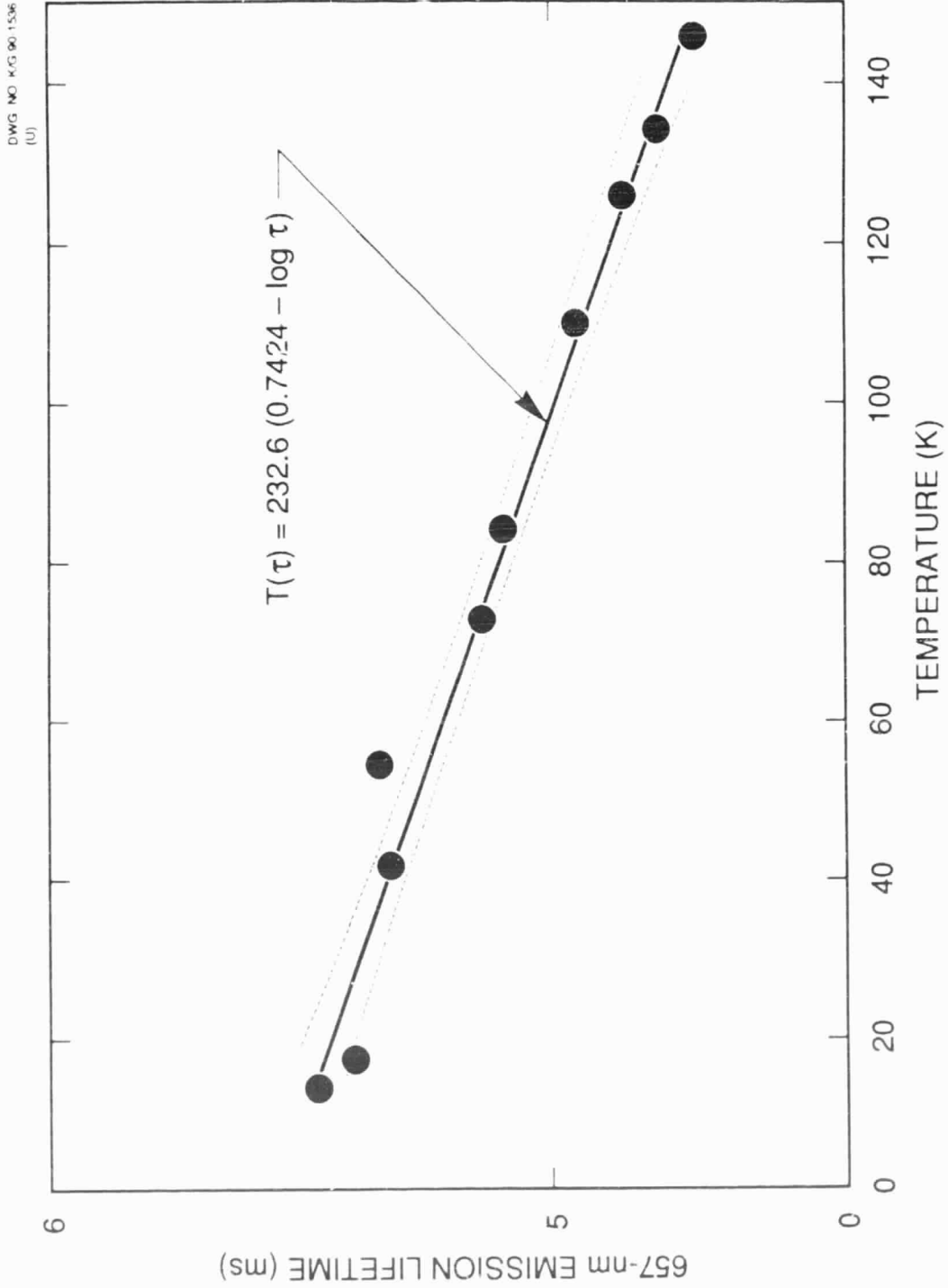
Fig. 12. Mg$_4$(F)GeO$_6$:Mn phosphor calibration.
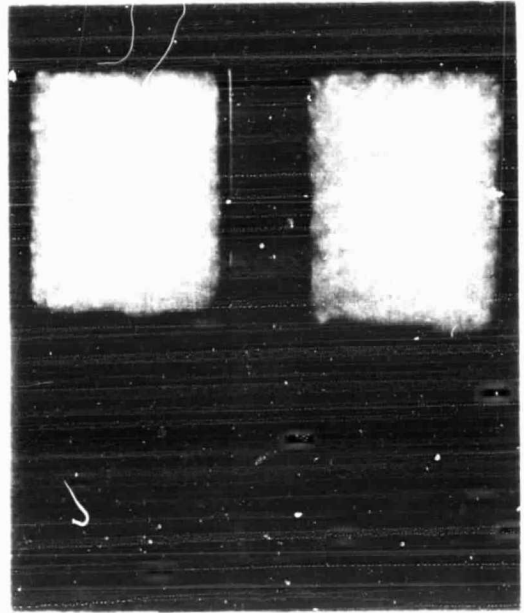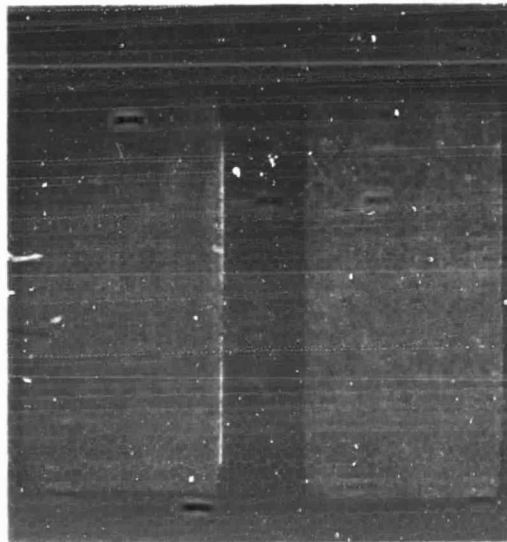
Fig. 13. Binder/phosphor (La$_2$O$_2$S:Eu) coupons excited by a UV light source. (a) Stycast 1266, (b) Stycast 1269, and (c) Sperex SP-115.

REFERENCES

1. C. M. Simmons, D. L. Beshears, and M. R. Cates, *Low-Temperature Phosphor Thermometry: Calibration of Europium-Doped, Lanthanum Oxysulfide Between Room Temperature and -194°C*, ORNL/ATD-25, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., February 1990.

2. W. H. Fonger and C. W. Struck, "Eu^{+++} ^{5}D Resonance Quenching to the Charge-Transfer States in Y$_2$O$_3$, La$_2$O$_2$S, and LaOCl," *J. Chem. Phys.* **52(12)**, 6364-6372 (June 1970).

3. S. W. Allison et al., *Rare-Earth Phosphors For Remote Thermographic Applications*, ORNL/ATD-12, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., April 1989.

4. M.R. Cates et al., *Remote Thermometry of Moving Surfaces by Laser Induced Fluorescence of Surface-Bonded Phosphor*, K/TS-11,232, Union Carbide Corporation, Oak Ridge Gaseous Diffusion Plant, November 1983, and *Proc. Laser Institute of America* **39**, 50-55 (1984).