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MARTIN MARIETTA

RARE-EARTH PHOSPHORS FOR REMOTE THERMOGRAPHIC APPLICATIONS

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April 1989

Applied Technology Division

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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ABSTRACT

Numerous phosphors with rare-earth dopants have emissions that are strongly dependent on temperature and are therefore useful for remote-temperature measurement, especially in moving, confined, or hazardous systems. The emission properties of various phosphors of this type were measured from room temperature to ~1200 °C, along with data relative to their stability under thermal cycling.

INTRODUCTION

The lighting and display industries use a variety of rare-earth-doped phosphors for various purposes. Some have been considered for or are used as laser media. These technologically important materials have emission properties that are temperature dependent. Consequently, we have been able to exploit them for a number of scientific and industrial thermometry applications. While most (if not all) phosphors exhibit a temperature dependence, we have concentrated on the rare-earth type in part because their spectra consist of sharply defined lines, which is a great advantage in several applications. Another reason for using them is because of the large base of research and development invested by industry and well reported in the literature.

We are interested in thermographic applications where standard devices, such as thermocouples and pyrometers, are either not usable or are less than optimal. Conditions such as these arise for rotating systems; systems in corrosive, vibrating, thermally fluctuating, or very hot environments; and systems with varying or unpredictable emissivity. In many of these situations, the ability to make a noncontact (or remote) measurement is highly desirable, if not necessary. Measurement examples would include rotating components in engines or generators, relatively cool surfaces in hot environments, surfaces that cannot be grooved or otherwise disturbed for thermocouple attachment, surfaces with layers of dissimilar material being eroded away, areas difficult to access with electrical wiring or areas in electrically noisy environments, and numerous other situations.

GENERAL DESCRIPTION OF PHOSPHOR-TEMPERATURE DEPENDENCE

Phosphors with a typical composition consisting of a metal oxide or oxysulfide doped with a rare-earth ion often have strong temperature dependence in the fluorescent emissions in certain parts of the spectrum. As an example, part of the visible emission spectrum of lanthanum oxysulfide doped with europium (La_2O_2S:Eu) is shown in Fig. 1. For this phosphor, around room temperature the group of lines near 467 and 512 nm have emissions strongly dependent on temperature. Emission strength decreases, reflected by a corresponding decrease in the decay time of the state, with increasing temperature. Figure 2 shows the decay-time effect for the 512-nm group. The temperature dependence arises because of strong competition between lattice de-excitation phonon processes and photon-emitting de-excitation within the dopant ion electronic levels.[1] For dopant ions whose electronic decays involve a variety of momentum and energy transitions, strong temperature dependencies can occur in different temperature bands for different emission wavelengths. The effect is illustrated in Fig. 3, where the total emission strengths for the types of D-level transitions vs temperature are shown. This single phosphor, then, could be used to monitor temperature over a range of several hundred degrees by selection of the appropriate emission wavelength. Other phosphors of this type also show this same wide-range temperature sensitivity.

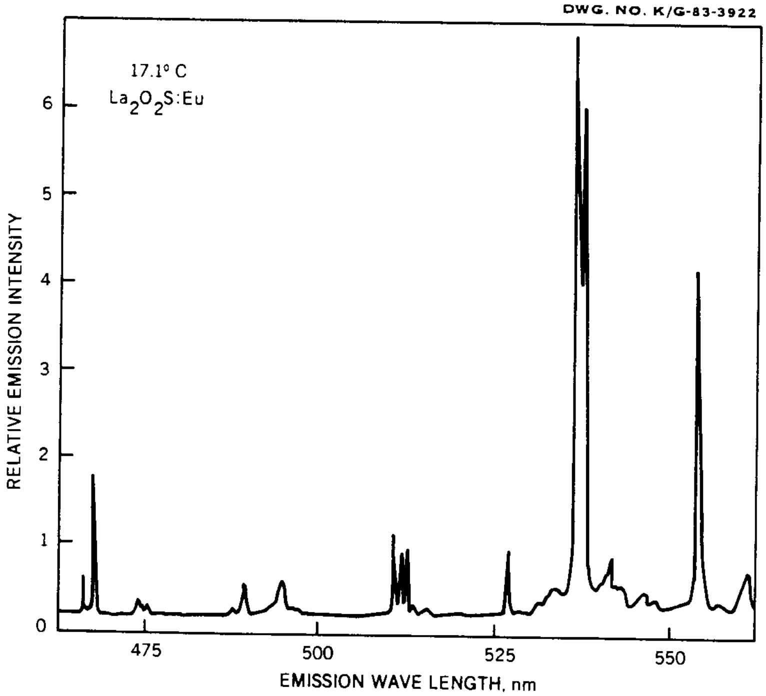

Fig. 1. Remote thermometry via phosphor luminescence.

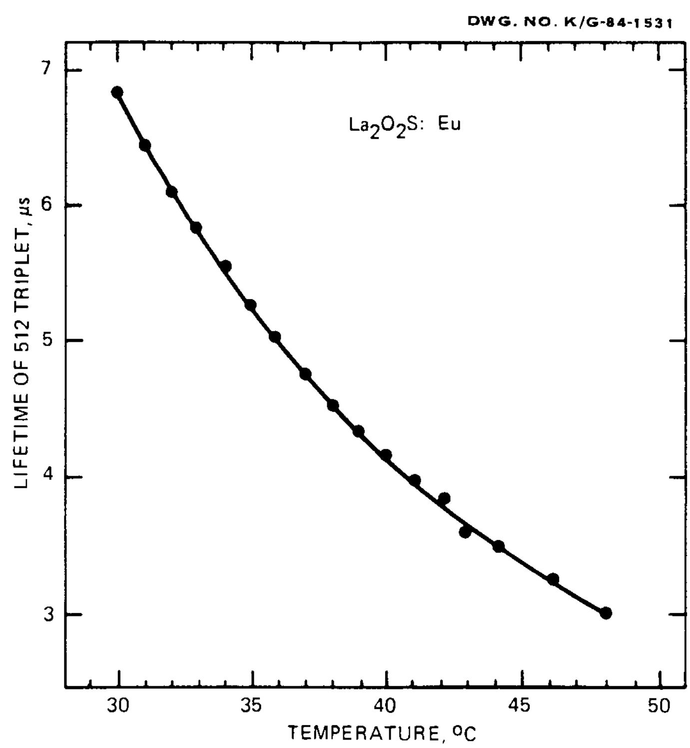

Fig. 2. Lifetime vs temperature.

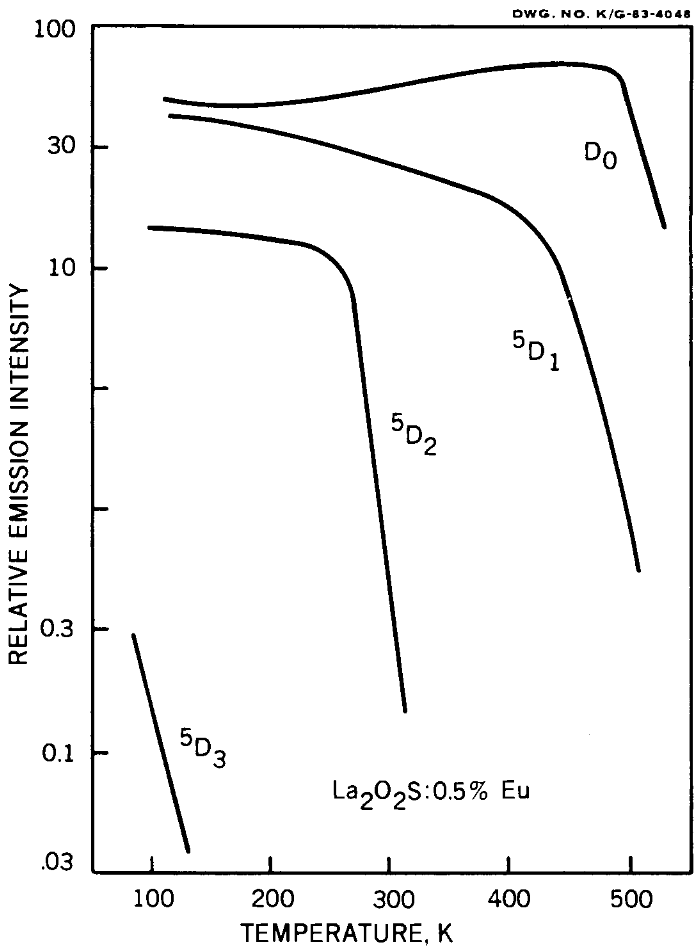

Fig. 3. Intensity vs temperature.

As observed in Figs. 2 and 3, the temperature effect can be very strong. In measurements with La_2O_2S:Eu, the temperature dependence near room temperature has been strong enough to allow determinations with <0.5°C uncertainty.[2] Decay-time measurement has been our method of preference for most applications. Details of the instrumentation systems we have used can be found in references 2 and 3. In this report, we will concentrate on summarizing the results of evaluating several phosphors over a wide temperature range.

EMISSION CHARACTERISTICS OF VARIOUS PHOSPHORS

This report describes part of the study of La_2O_2S:Eu, Y_2O_2S:Eu, Y_2O_2S:Tb, YVO_4:Eu, YVO_4Dy, Y_2O_3:Eu, and Y_2O_3:Gd. Several other phosphors are also under active study. The properties measured were excitation and emission spectra and fluorescent decay times (of selected lines) as a function of temperature.

EUROPIUM-DOPED PHOSPHORS: EMISSION CHARACTERISTICS

The characteristic line spectrum seen in Fig. 1 for La_2O_2:Eu is typical of that for any of the phosphors with this dopant ion. The D-to-F (see reference 1) transitions are dominant in the visible spectrum, and their relative strengths are partly a function of the lattice. The appearance of the fluorescence varies from green to red, depending on the host lattice and the dopant concentration. The variation occurs because of the differing relative strengths of the ^5D transitions (see Fig. 3). The effect of the host lattice is illustrated by comparing Fig. 4, the emission spectrum from Y_2O_3:Eu, with the Y_2O_2S:Eu spectrum in Fig. 5. In Fig. 4, the strength lies almost entirely in $^5D_0$ transitions, which occur in the yellow and red. The resultant color for Y_2O_3:Eu, then, is reddish orange; for Y_2O_2S:Eu, yellow. By comparing the two spectra in Fig. 5a and b, the dopant effect is observed. The 0.1% europium dopant concentration produces a higher proportion of $^5D_2$ and $^5D_1$ transitions compared with the 1.0% concentration, shifting the color toward the blue. The dopant effect is discussed by Ozawa and Jaffe.[4] Basically, when dopant ions are widely spaced in the lattice, few dopant-dopant interactions take place. These dopant-dopant interactions tend to cause electrons to move to lower-lying electronic levels before undergoing the final transition to the ground state configuration. The lower-lying levels produce longer (redder) wavelengths.

Fig. 6 shows decay times vs temperature for selected europium ion wavelengths for La_2O_2S< YVO_4, and Y_2O_3. These materials produced the brightest and stablest phosphors from among the group evaluated (see Temperature-Cycling Behavior). Figure 6 shows the strong temperature dependence and the shift of temperature range in which that dependence is strong that occurs with change of host for the dopant ion. It is clear that for just these three phosphors, a significant part of the temperature range from ~ 0 to 1200 ° C can be monitored.

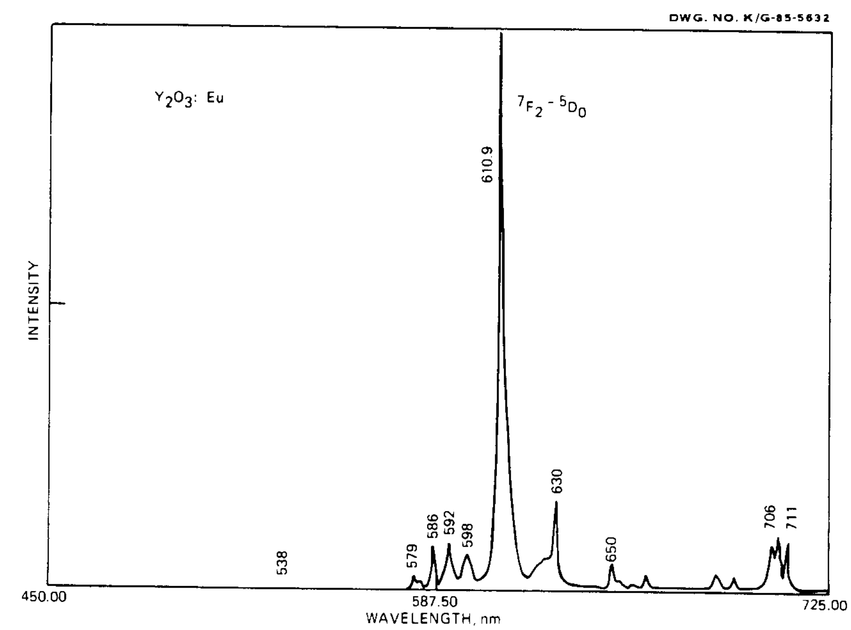

Fig. 4. Fluorescence spectrum of strongest lines.

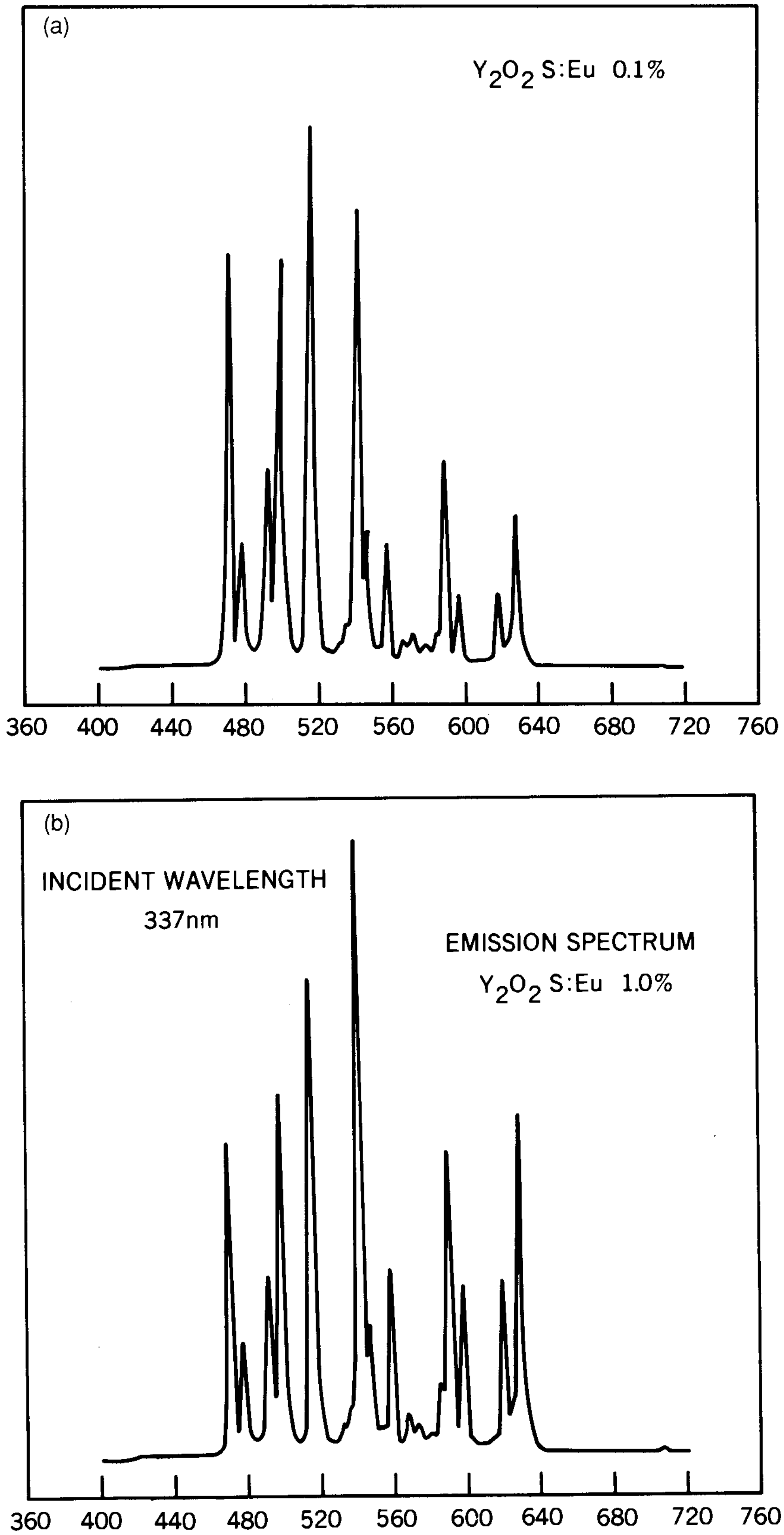

Fig. 5. Emission of spectra of Y_2O_2S:Eu.
(*a*) 0.1% dopant concentration, (*b*) 1/07% dopant.

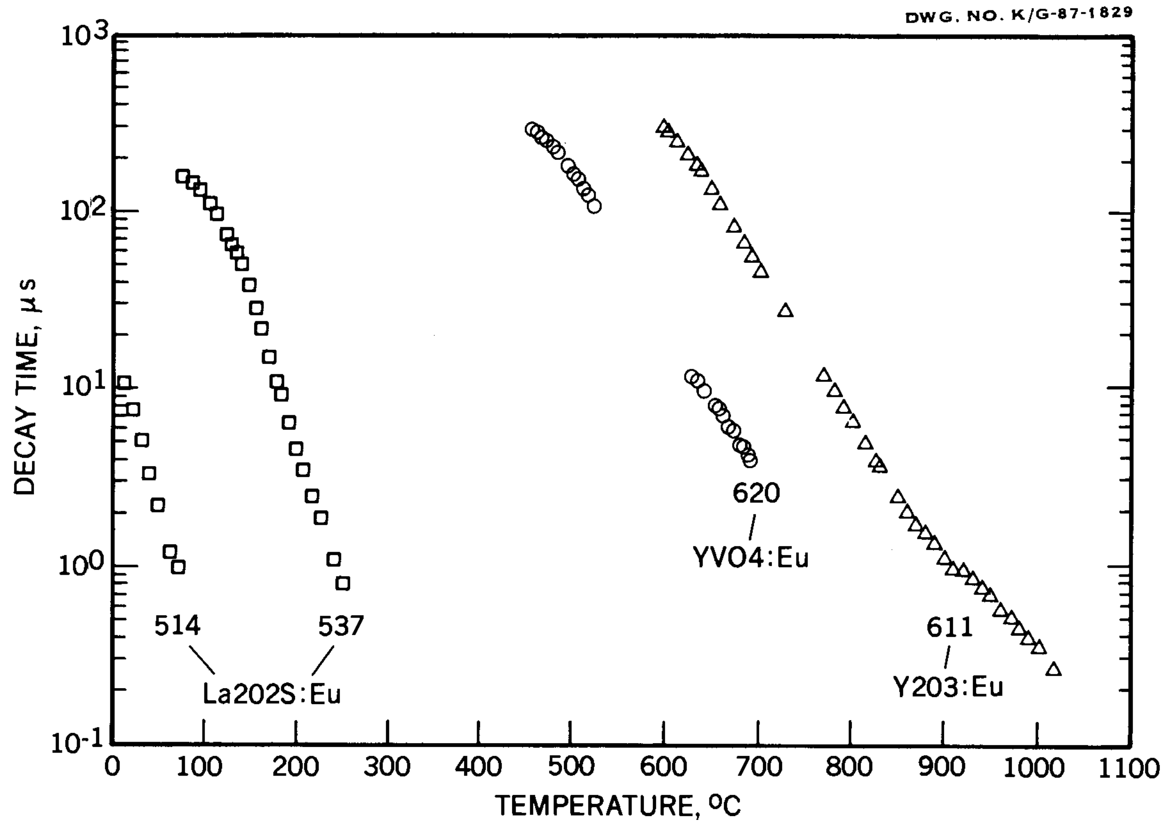

Fig. 6. Decay time vs temperature for several phosphors.

EXCITATION CHARACTERISTICS

Figure 7 shows the excitation function of Y_2O_3:Eu for emission at 611 nm. The dopant concentration was 6.8%. This figure is representative of the excitation characteristics of rare-earth-doped phosphors. The broad band in the ultraviolet (UV), called the charge-transfer band,[1] shows the region of most efficient excitation for UV sources. The peaks at longer wavelengths are produced by resonances associated with electronic transitions from the Eu^{+++} ground state configuration to states near the level from which the 611-nm emission occurs. Excitation spectra provide data needed to determine relative fluorescence strengths for the specific laser or other light source used. They also show temperature effects, especially in the broadening of the charge transfer band. A future publication[5] will discuss this temperature behavior for Y_2O_3:Eu.

EMISSION CHARACTERISTICS OF OTHER PHOSPHORS

Aside from the fact that the europium dopants alone probably will inadequately cover every temperature range of interest, there are other measurement situations that give good reason to use phosphors with other dopants. For example, when two or more layers of phosphor are used to study temperature gradients, it is very important to use the wavelength emissions from different dopants as discriminators for the various layers. Or, a mixture of

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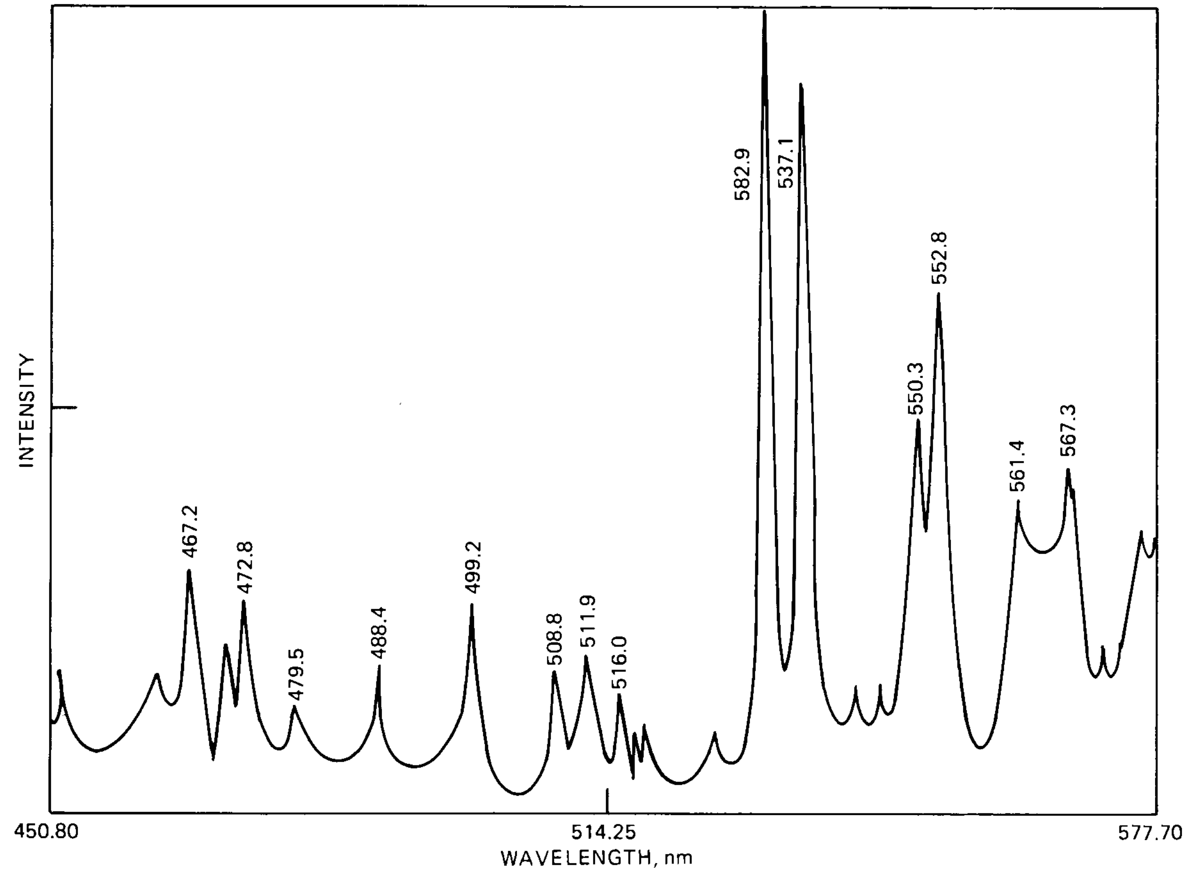
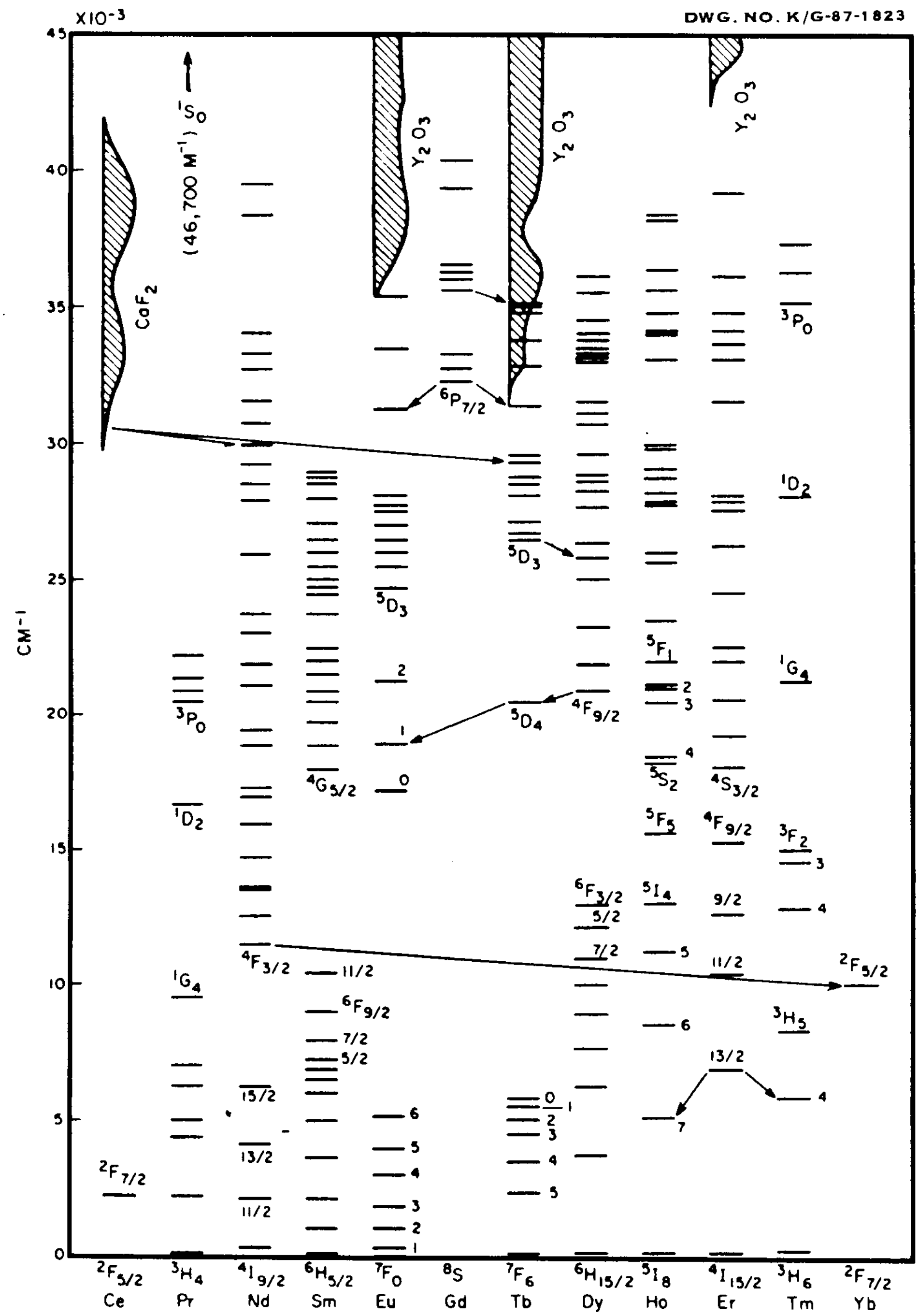


Fig. 7. Excitation spectrum.

phosphors--with each phosphor's emission characteristic appropriate for a certain temperature region--may be the most attractive way to cover a large temperature range. Possibly, some particular dopant and lattice not among the group of europium phosphors may have an optimal temperature dependence or emission intensity for the particular application. Consequently, we also studied terbium-, gadolinium-, and dysprosium-doped phosphors in a broad search for useful fluorescent materials.

As a kind of summary of the types of emissions to be expected from the rare-earth dopants, Fig. 8 shows a table of low-lying electronic levels[6] for the various ions. Transitions among these levels produce the characteristic fluorescence signatures of the phosphors. Gadolinium, for example, has very large energy difference between ground state and first-excited state bands and gives rise to emissions centered in the near UV. The strongest emission line we measured in studying Y_2O_3:Gd was at 313 nm. The peak excitation wavelength (above 220 nm) was at ~275 nm. The terbium ion is well known for its green emission coming from transmissions from the $^5D_4$ level to the ground-state configuration. In Y_2O_2S:Tb, we observed a strong peak at 545 nm and several other smaller peaks between 491 and 622 nm. The 545 line has strong temperature dependence in the 300 to 600°C region, a range over which we have done careful calibration of the decay time vs temperature. For further information and details, Blasse[7] gives excellent discussions of the fluorescence behavior of the common rare-earth dopant ions.

Representative of the data from the group of phosphors with other than Eu^{+++} dopants is the information in Fig. 9 summarizing some of the properties of YVO_4:Dy. The main groups of dysprosium emissions are shown in the top view. The data are recorded on an optical multichannel analyzer and show temperature as a parameter. The bottom part of the figure shows a plot of amplitude ratio vs temperature of the two lines toward the



Source: P. G. Goldberg, ed., *Luminescence of Inorganic Solids,* Academic Press, New York, 1966.

Fig. 8. Energy levels of lanthanides.

blue end of the spectrum. This not only illustrates the strength of the temperature dependence up to ~400 °C but shows another important way in which the fluorescence data can be used. The line radio method is important in cases where the stimulating radiation is continuous, in situations of dynamic temperature increase or decrease, in two-dimensional measurements, and other situations where decay-time monitoring has some limitation.

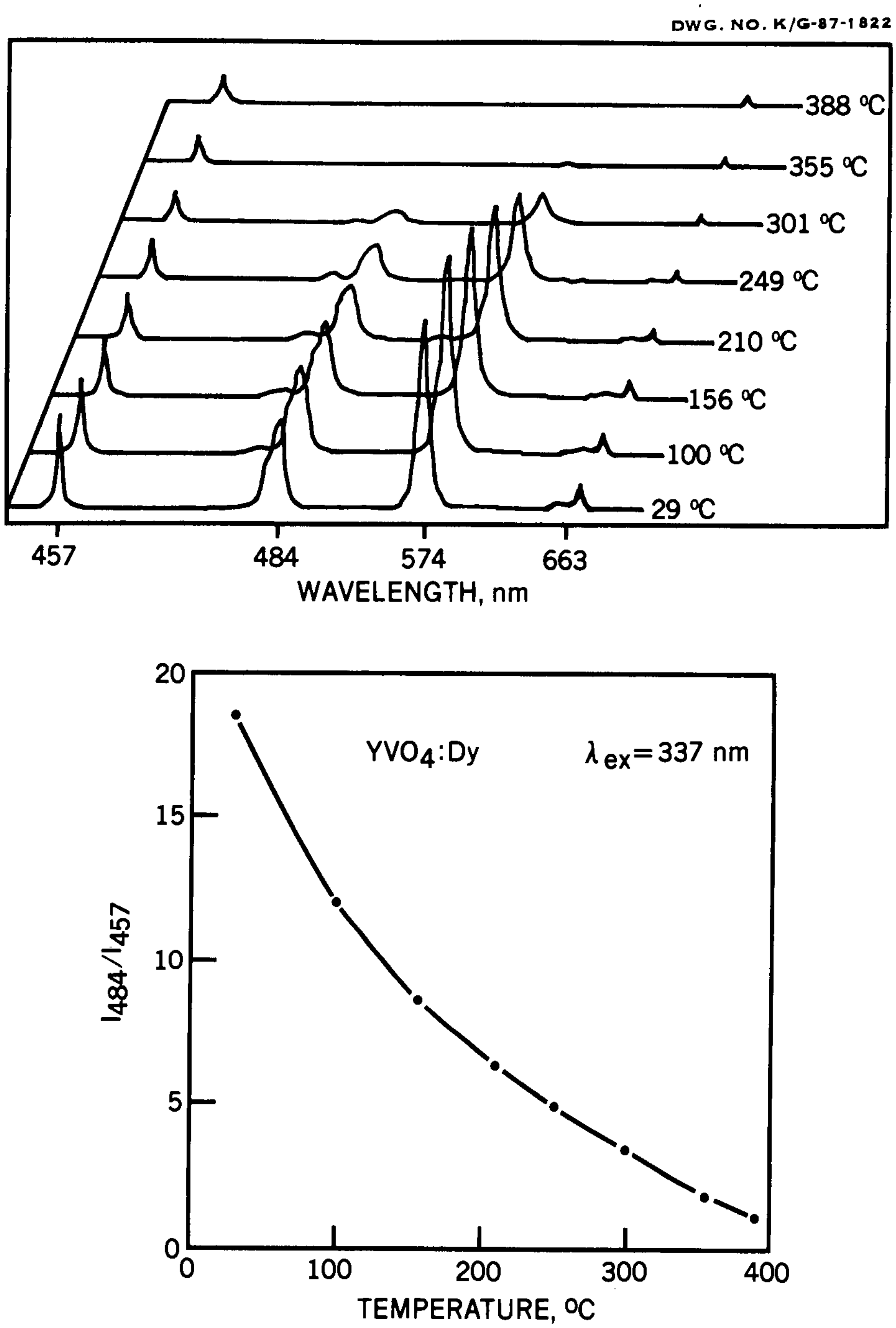


Fig. 9. Temperature dependance of YVO_4:Dy.

TEMPERATURE-CYCLING BEHAVIOR

For practical temperature-monitoring applications, thermographic phosphors must remain relatively stable under the conditions they must experience during the measurement. One important consideration, then, is any change in fluorescent properties that might accompany temperature cycling. Such cycling is likely to occur in machinery that is turned off and on many times and undergoes large temperature excursions when this occurs. Good examples are turbine engines, production furnaces, compressors, or other devices that undergo temperature excursions. In connection with this concern, we evaluated all the phosphors temperature-cycling in this study. Representative of numerous sets of data is the information shown in Figs. 10 and 11. In Fig. 10, for Y_2O_2S:Eu, there was a significant variation of fluorescent response from run to run in a laboratory setup where measurement procedures and conditions remained practically unchanged. The variation can occur because of dopant-ion-concentration changes by ion migration, from chemical breakdown of the phosphor, or perhaps from a configuration change in the lattice. The phosphors from this that had the most stable behavior under cycling were La_2O_2S:Eu, YVO_4:Eu, Y_2O_3:Eu, and YVO_4:Dy. The Y_2O_3:Gd work is not complete. The Y_2O_2S:Tb and Y_2O_2S:Eu showed significant fluctuations. Figure 11 shows cycling data for La_2O_2S:Eu. Here the phosphor response is stable and repeatable to within the limits of the measurement system.

Temperature-cycling evaluation is part of a larger aspect of our work, which includes the general area of bonding phosphors to various surfaces of interest in thermography applications. Progress in this area will be reported in future publications.

SUMMARY OF RESULTS

Table 1 summarizes the results of the fluorescence study for the listed phosphors. Further work is being done on all these materials. This continuing activity and that for other phosphors will be reported in a timely manner upon its completion.

ACKNOWLEDGMENTS

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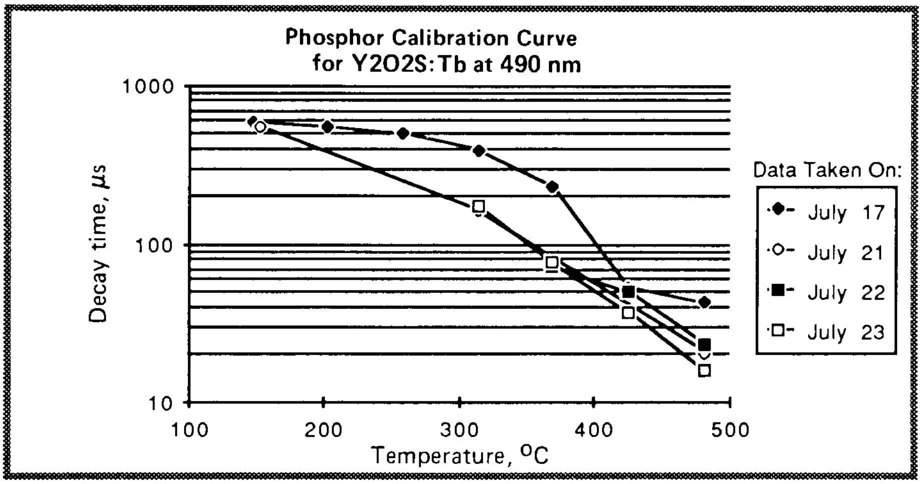

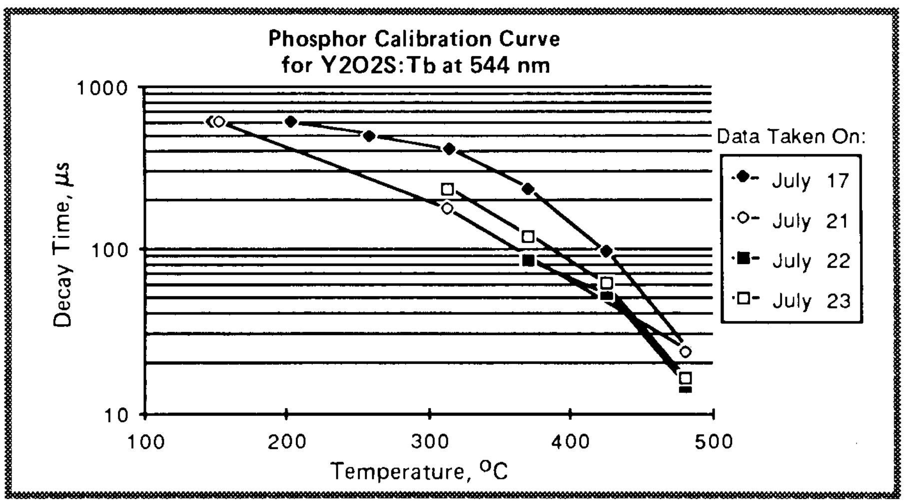

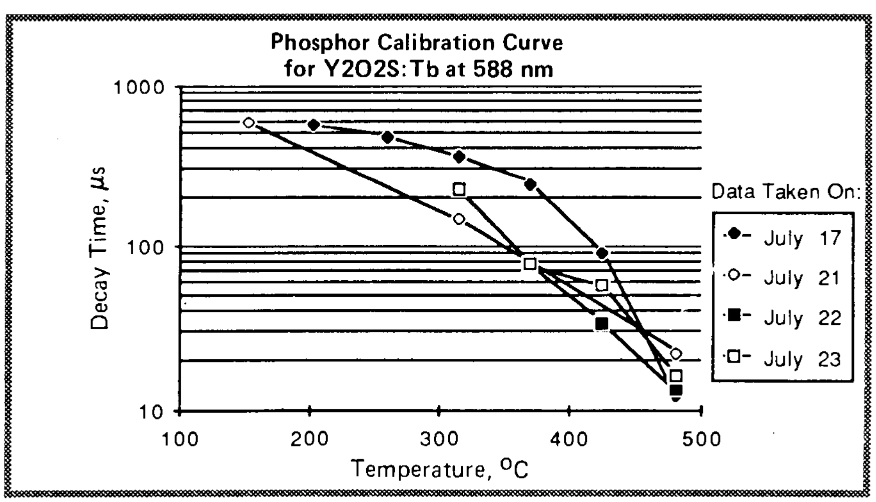

Fig. 10. Temperature cycling data for Y_2O_2S:Tb.

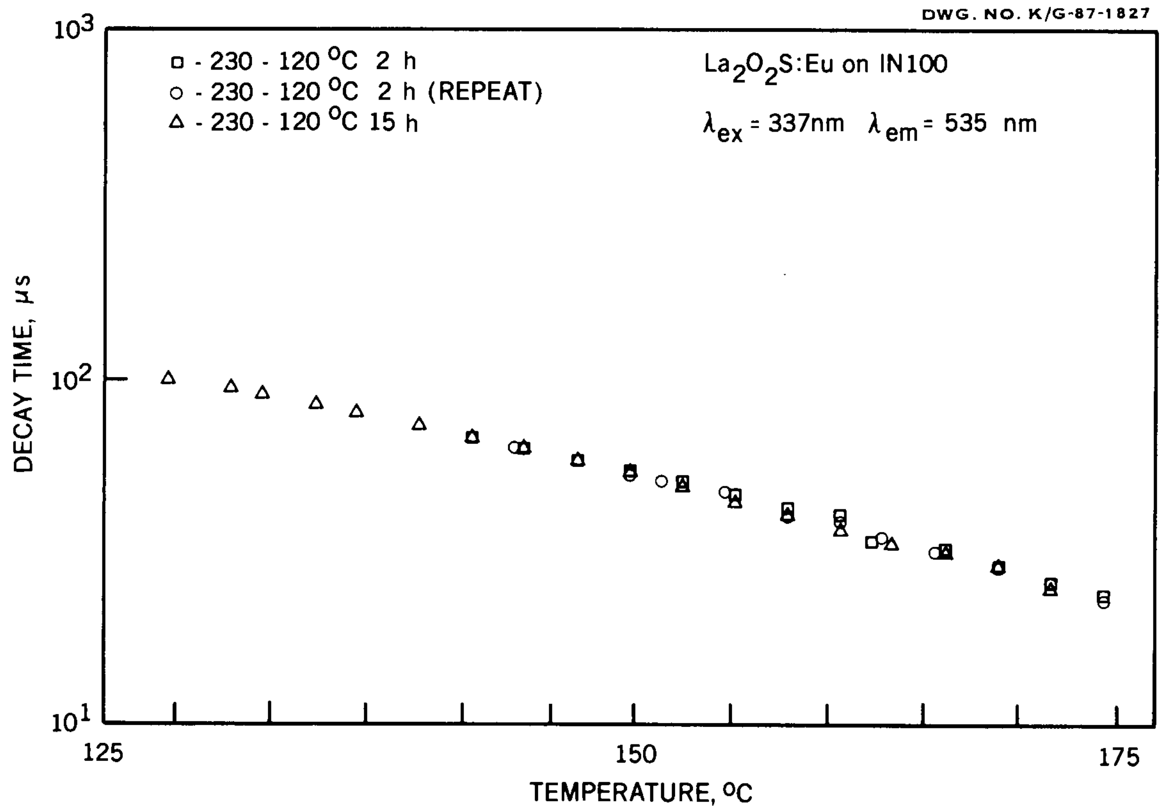

Fig. 11. Temperature cycling behavior of La_2O_2S:Eu.

Table 1. Summary table of thermographic phosphors

Phosphor formula	Wavelengths studied (nm)	Measured range (°C)	Thermal stability
La_2O_2S:Eu	467, 514, 537, 624	-200-300	Good
Y_2O_2S:Eu	514, 537, 624	30-300	Poor
YVO_4:Eu	625	400-700	Good
Y_2O_3:Eu	611	700-1200	Good
Y_2O_2S:Tb	490, 544, 588	100-500	Poor
YVO_4:Dy	457, 484, 575	50-400	Good
Y_2O_3:Gd	313	Undetermined	Undetermined

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