**LOW-TEMPERATURE PHOSPHOR THERMOMETRY:
CALIBRATION OF EUROPIUM-DOPED LANTHANUM OXYSULFIDE
BETWEEN ROOM TEMPERATURE AND -194°C**

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CONTENTS

	<u>Page</u>
LIST OF FIGURES	iii
ABSTRACT	iv
INTRODUCTION	1
DISCUSSION	
EUROPIUM-DOPED, LANTHANUM-OXYSULFIDE	
TEMPERATURE DEPENDENCE.	1
SETUP FOR LOW TEMPERATURE MEASUREMENTS.	7
COLLECTING AND ANALYZING THE LOW	
TEMPERATURE DATA	7
CONCLUSION	7
ACKNOWLEDGMENT	10
REFERENCES	11

LIST OF FIGURES

<u>Fig. No.</u>	<u>Title</u>	<u>Page No.</u>
1	Phosphor Emission Spectrum from $\text{La}_2\text{O}_2\text{S:Eu}$ at 21.2°C Between 450 and 670 nm	2
2	Phosphor Emission Spectrum from $\text{La}_2\text{O}_2\text{S:Eu}$ at 100°C Between 450 and 670 nm	3
3	Phosphor Excitation Spectrum for $\text{La}_2\text{O}_2\text{S:Eu}$ at 21.2 and 115°C	4
4	Temperature Dependence for the ^5D Emissions of $\text{La}_2\text{O}_2\text{S:Eu}$	5
5	Energy Levels In Europium $3+$ with the Charge-Transfer State in $\text{La}_2\text{O}_2\text{S}$	6
6	Schematic of Low Temperature Calibration Setup for $\text{La}_2\text{O}_2\text{S:Eu}$	8
7	$\text{La}_2\text{O}_2\text{S:Eu}$ Phosphor Temperature Calibration	9

ABSTRACT

Remote-temperature measurements can be accomplished by inducing fluorescence in doped phosphors and measuring emission lifetimes. Some phosphors have been calibrated for high temperature measurement from room temperature to about 1200°C and are proving useful where remote sensing is required. Attention is now turned to remote thermal sensing at low-temperature ranges. Because it has strong emission spectra at low temperatures, as well as relatively high temperatures, lanthanum oxysulfide ($\text{La}_2\text{O}_2\text{S:Eu}$) is now being calibrated at low temperatures. The temperature range of concern in this paper is from about -194°C to room temperature.

INTRODUCTION

Surface temperatures of moving objects or any object restricted from direct contact with a thermal probe can be very difficult to measure. One way to accomplish this is to coat a small area of the surface to be measured with a rare-earth doped phosphor and induce fluorescence by excitation with ultraviolet radiation. The emission lifetime and intensity at certain wavelengths are directly dependent on temperature. Studies with various doped phosphors at high temperatures have been effected with great success and have added a new dimension to thermometry. A need for this remote thermal ability at low temperatures exists in areas such as space vehicles and exploratory machinery. This paper will investigate the use of lanthanum oxysulfide doped with europium ($\text{La}_2\text{O}_2\text{S:Eu}$) for measuring temperatures from about -194°C to room temperature.

DISCUSSION

EUROPIUM DOPED LANTHANUM OXYSULFIDE TEMPERATURE DEPENDENCE

The visible emission spectra at two different temperatures from 450 to 670 nm wavelengths for $\text{La}_2\text{O}_2\text{S:Eu}$ are shown in Figs. 1 and 2. The excitation spectrum for $\text{La}_2\text{O}_2\text{S:Eu}$ is shown in Fig. 3 for 21.2 and 115°C . Fonger and Struck found that the ^5D emissions of Eu^{3+} in $\text{La}_2\text{O}_2\text{S}$ quench sequentially with increasing temperature in the simple order $^5\text{D}_3$, $^5\text{D}_2$, $^5\text{D}_1$, $^5\text{D}_0$.¹ Fonger and Struck showed that the emission intensity for each of the quenched states has a temperature dependency shown in Fig. 4. Emission strength decreases with a corresponding decrease in decay time of the state with increasing temperature. The strong temperature dependence exists because of competition between nonradiative-lattice de-excitation processes and photon-emitting de-excitation within the europium ion electronic levels. The europium ions have electron decays which encompass a variety of momentum and energy transitions thus giving rise to strong temperature dependencies in different temperature bands for different emission wavelengths. The emission lines come from transitions between the ^5D levels and the ^7F levels of the ground state. This effect is illustrated in Fig. 5 where the emission strengths for the D-level type transitions vs temperature are shown.^{2,3}

Measurements with $\text{La}_2\text{O}_2\text{S:Eu}$ near room temperature have exhibited such strong temperature dependency as to allow determinations with $<0.5^\circ\text{C}$ uncertainty.³ $\text{La}_2\text{O}_2\text{S:Eu}$ could be used to measure over a wide (several hundred degrees) range. The main objective of this report is to present the data which have been collected on $\text{La}_2\text{O}_2\text{S:Eu}$ at temperatures ranging from room temperature down to liquid nitrogen temperature (about -194°C).

Fig. 1. Phosphor emission spectrum from $\text{La}_2\text{O}_2\text{S}:\text{Eu}$ at 21.2°C between 450 and 670 nm.

Fig. 2. Phosphor emission spectrum from $\text{La}_2\text{O}_2\text{S}:\text{Eu}$ at 100°C between 450 and 670 nm.

Fig. 3. Phosphor excitation spectrum for $\text{La}_2\text{O}_2\text{S:Eu}$ at 21.2 and 115°C.

Fig. 4. Temperature dependence for the $5D$ emissions of $\text{La}_2\text{O}_2\text{S}:\text{Eu}$.

Fig. 5. Energy levels in europium 3+ with the charge-transfer state in $\text{La}_2\text{O}_2\text{S}$.

SETUP FOR LOW TEMPERATURE MEASUREMENTS

A schematic of the setup is shown in Fig. 6. A pulsed nitrogen laser (337 nm) was used to produce the excitation signal for the phosphor. The signal was carried from the laser by way of an optical fiber (600 μm diam, plastic-coated silica) to the sample which consisted of a thin, packed film of $\text{La}_2\text{O}_2\text{S:Eu}$. The sample was housed in a small brass holder along with two thermocouples. The brass holder was then placed inside a Teflon carrier which could be lowered and raised incrementally in the cold reservoir. The cooling liquids used to attain the various temperatures were liquid nitrogen, frozen carbon dioxide and methanol mixture, and ice water.

The fluorescent emission signal was picked up by the same type of optical fiber mentioned earlier 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.

COLLECTING AND ANALYZING THE LOW TEMPERATURE DATA

Several runs were made in each temperature range and each temperature datum was repeated four times for a good average. This calibration study has concentrated on a temperature range between room temperature and liquid nitrogen temperature (about -194°C). The emission lines representing the $^5\text{D}_2$ transition (see Fig. 4) near 467 and 512 nm were investigated. The $^5\text{D}_3$ transition emission lines near 434 nm were also examined.

The $^5\text{D}_1$ and $^5\text{D}_0$ lines near 538 nm and 624 nm, respectively, were examined as controls, because they do not exhibit temperature dependency in this temperature range. The data are plotted in Fig. 7 as the temperatures in degrees Celsius vs the log of the emission lifetimes in microseconds. The temperature dependency of the 514 and 434-nm lines is clearly exhibited.

CONCLUSION

Just as in high temperature thermometry, oxysulfides doped with rare-earth ions such as europium-doped lanthanum oxysulfide, can be used for remote low temperature sensing. Moving, inaccessible, or hazardous cold environments can be thermally investigated using these phosphor techniques.

Additional research is needed to fully exploit the potential in this area. Different phosphors and rare earths should be investigated. A logical next step would be investigating the thermal characteristics produced with bonding $\text{La}_2\text{O}_2\text{S:Eu}$ to a surface of interest and extending the calibration of the $^5\text{D}_3$ transition state to lower temperatures using liquid helium.

Fig. 6. Schematic of low-temperature calibration setup for La₂O₂S:Eu.

Fig. 7. $La_2O_2S:Eu$ phosphor temperature calibration.

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