OPTIMIZATION OF THE MgS:Eu:Sm PHOSPHOR FOR POTENTIAL USE AS AN OPTICALLY STIMULATED PERSONNEL DOSIMETER

by

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(ABSTRACT)

Magnesium sulfide activated with europium and samarium is a candidate phosphor for laser stimulated personnel dosimeters. Optically stimulated luminescence (OSL) dosimeters are advantageous in that they provide a faster, isothermal dose measurement than conventional thermoluminescent dosimeters.

The effects of activator concentration and chemical substituents are examined in order to increase OSL intensity, improve the OSL emission wavelength and to increase the chemical stability of the MgS lattice.

In addition, UV photoluminescence and thermoluminescence of the MgS:Eu:Sm phosphor was investigated to improve the understanding of the optical processes in MgS:Eu:Sm phosphors.

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1. INTRODUCTION

Rare earth-doped magnesium sulfide is an excellent candidate material for optically stimulated dosimeter phosphors. With the decreasing cost and increasing availability of intense infrared lasers, materials exhibiting optically stimulated luminescence (OSL) are being examined for use in personnel dosimeters.

OSL is a two-step process. First, ultraviolet radiation excites electrons from the valence band to a metastable excited state known as a trap, associated with a lattice impurity or defect. Electrons in the trap are forbidden by electrostatic forces from atoms of the surrounding crystal from returning to the valence band unless initially excited to a higher energy state or to the conduction band. Secondly, when the phosphor is stimulated by infrared radiation (i.e., from a YAG:Nd^{3+} laser), the electrons in the traps are released and allowed to return to the ground state of the luminescence center accompanied by the release of visible light. The intensity of this light emission is proportional to the number of quanta of ionizing radiation absorbed.

Optically stimulated luminescence in personnel dosimeters has a number of advantages over conventional thermoluminescent dosimeters.

1.) OSL dosimeters use photon energy rather than thermal energy to release the electrons from the trapping states. Thus, the decrease in luminous intensity with thermal cycling is avoided and the luminescent crystals will have a constant response regardless of the number of times the traps are emptied.

2.) Optical release of electrons from traps may be activated by a pinpoint laser on a small area. The remainder of the surface of the dosimeter continues to count quanta of ionizing radiation. A cumulative record of radiation exposure over a long time period may be kept by selectively deactivating electron traps on one portion of the dosimeter while allowing other sections to continually absorb radiation.

3.) Optical release of electrons from the traps may be accomplished much faster than thermal release from the traps, with detrapping times of less than 50 nanoseconds reported.

Magnesium sulfide doped with divalent europium and trivalent samarium is a candidate phosphor for OSL personnel dosimeters. The trivalent samarium has trapping states which are sufficiently below the conduction band to allow 1.06 μm radiation from a YAG:Nd^{3+} laser to free the electrons from the traps and allow them to return to the ground state. Magnesium sulfide, in addition, has a favorable effective atomic number ($Z_{eff.}$ = 14.5), close to that of human tissue. The low $Z_{eff.}$ is important in that the sensitivity of the phosphor to low levels of radiation closely matches the sensitivity of human tissue.

The MgS host lattice is highly susceptible to degradation in moist atmospheres, reacting spontaneously with water at room temperatures. The reaction products include the toxic gas H_2S. For practical dosimetry purposes it is necessary to either isolate the material from the atmosphere or to stabilize the lattice by the addition of substituent cations or anions.

The objectives of this research are to:

1.) Achieve a high brightness and favorable emission wavelength for the optically stimulated emission of the $(Mg_{1-x-y},Eu_x,Sm_y)S$ phosphor.

2.) Improve the ability of this phosphor to count quanta of ionizing radiation by populating trapping states with electrons.

3.) Improve the resistance of the $(Mg_{1-x-y},Eu_x,Sm_y)S$ phosphor to moisture induced degradation by the incorporation of substituent cationic species into the MgS lattice.

II. LITERATURE SURVEY

A. Alkaline Earth Sulfide Phosphors.

Alkaline earth sulfides were among the first known class of phosphor materials. In the nineteenth century, Lenard conducted an extensive study of this family of phosphors. However, until recently, alkaline earth sulfides have been neglected due to hydrolysis effects when exposed to atmospheric moisture and to the poor reproducibility of their luminescent properties.[23,24]

All of the alkaline earth sulfides crystallize in the simple cubic (halite) structure. They are highly ionic in character due to the large electronegative difference between the alkaline earth cation and the sulfide anion. As a result, the alkaline earth sulfides are insulators with large energy gaps. MgS has an energy gap (E_g) of 5.4eV.[11]

The large energy gaps are responsible for the plethora of different dopant ions which may serve as activators for these phosphors. Lehmann (1971) revealed that 31 different elements may activate CaS phosphors.[7,13,22] The high band gaps enable substituent ions to form sparsely spaced energy levels within the band gap, thus increasing the number of possible radiative electron transitions which may occur. Materials with a lower band gap will decrease the spacing between energy levels increasing the probability of non-radiative electron decay with the subsequent production of phonons.

B. Lanthanide Cation Activators in Alkaline Earth Sulfides.

Selected lanthanide group cations have been shown to be excellent activators in a wide variety of different host lattices, including the alkaline earth sulfides. A number of the lanthanide ions have unfilled 4f energy states allowing electrons to be easily excited from 4f states of lower energy to 4f states of higher energy. The energy gaps between 4f states are favorable for the emission of visible light on the return of the electron to a lower state.

Trivalent lanthanide cations such as Eu^{3+}, Sm^{3+}, Tb^{3+} and Dy^{3+} are known as line emitters, because of their nearly monochromatic emission lines under ultra-violet excitation.[4] This is due to the shielding of the 4f electrons in the activator from the electric field caused by the atoms in the surrounding lattice. Electrons in unshielded orbitals will be subjected to the electrostatic crystal field, creating bands of energy levels where a single energy level will be in a free ion. This results in UV emissions which span a range of wavelengths or "emission bands".[25]

Yamashita and Asano[15] investigated the UV emission and excitation spectra of $MgS:Sm^{3+}$ at 30^{o}K where Sm^{3+} behaves as a line emitter. The sharpest lines are associated with $^{6}H_{7/2}$ transitions between 4f states centered at 610.3 nm and

657.1 nm respectively. The excitation spectra show a plethora of weak lines in the range from 370 to 550 nm associated with 4f→4f transition, the largest peak being at 395 nm. Wide excitation bands appear at 317 nm and 272 nm associated with 4f⟶5d transitions, leading the investigators to conclude that electrons are excited into 5d orbitals where they decay non-radiatively to the lowest 5d orbital. From this electron state, they decay to any of the 4f levels producing the line emissions.

Divalent rare earth ions such as Eu^{+2} show emission bands in alkaline earth sulfides, due to 5d→4f transitions, under ultraviolet excitation. The 5d orbitals are not shielded from the crystal field as are the 4f orbitals, thus emission bands occur for Eu^{2+} doped alkaline earth sulfide phosphors.

Nakao[9] studied the UV emission and excitation spectra for Eu^{+2} ions in MgS at 300 K, and revealed a single narrow emission band centered around 592 nm. The position and shape of this emission band remains the same despite variations in Eu^{2+} ion concentration up to 1 mole % or variations in excitation wavelength from 250 nm to 500 nm radiation. Nakao concluded that the emission resulted from a single Eu^{2+} ion center, rather than aggregate centers. At concentrations exceeding 0.1 mole percent a third small emission band appears at 280 nm.

Excitation spectra reveal two primary excitation bands at 482 nm and 253 nm, characteristic of $4f^7 \longrightarrow 4f^65d^1$ transitions, with the 5d band split by an octahedral crystal field.

C. The Nature of Electron Trap Formation in Lanthanide Doped Alkaline Earth Sulfides.

Electron traps are excited electron states, associated with lattice defects or impurities in which an electron is forbidden by the electrostatic forces of surrounding atoms from returning directly to the valence band. Electron-hole recombination may occur only if the trapped electron is initially excited thermally or optically out of the trapping state into the conduction band or into an excited state of the luminescence center. Recombination is then allowed at the luminescence center accompanied by the release of a photon. Thermal stimulation of the electron from the trapping state is known as thermoluminescence. Optical stimulation of the electron is known as optically stimulated luminescence.

Alkaline earth sulfides show thermoluminescence with a wide variety of dopants, and in some instances, without any activators being present.[26,28] This suggests that the trapping states may be related to intrinsic defects in addition to specific activator ions.

Ghosh and Shankar[6] investigated pure CaS for point defects by electron paramagnetic resonance (EPR). Two types of intrinsic defects were discovered and ascribed to a S^{2-} vacancy coordinated with six Ca^{2+} ions and a S^{2-} vacancy coordinated with five Ca^{2+} ions and a Ca^{2+} vacancy. The sulfur vacancy has an effective positive charge and serves as an electron trap analogous to an F center in alkali halides.

Rao[11] studied the doubly activated phosphor $CaS:Bi^{3+}:Cu^{1+}$, and from the results of electrical conductivity and dielectric constant measurements, concluded the that thermoluminescence arose from neutral complexes such as $[Bi_{Ba} - V_{Ba} - Bi_{Ba}]^{o}$ $[Cu_{Ba} - V_{s} - Cu_{Ba}]^{o}$ and $[Bi_{Ba} - Cu_{Ba}]^{o}$.*

Chakrabarti[16] investigated the mechanism of charge balance when trivalent lanthanides substitute for Mg^{2+} in MgS, and postulated that for two trivalent cations, an Mg vacancy (V_{Mg}) would result. Upon irradiation, this vacancy may capture a hole forming a V^{-} center complex, ($V_{Mg} + e^{+} + S^{-2}$). The low temperature thermoluminescence peak (80°C-100°C) is believed to be due to the release of the electron hole from the V^{-} center accompanied by recombination luminescence.

* the symbols $[A_B - V_B - C_B]$ indicate associated point defects. V_B denotes a B atom vacancy, whereas A_B indicates an A atom in the B site. The point defects do not necessarily have to be adjacent, but must be near enough to allow an electron to tunnel from one point defect the other. The superscript on the right indicates the charge of the complex.

Keller, Mapes and Cheroff[17] hypothesized that the trapping states in alkaline earth sulfide phosphors containing Eu^{2+} and Sm^{3+} were due to Sm^{3+} that had captured an electron, with the corresopnding hole being trapped at the Eu^{2+}

$$Sm^{3+} + e^{-} \rightarrow Sm^{2+}$$

$$Eu^{2+} + e^{+} \rightarrow Eu^{3+}$$

Upon optical stimulation, the electron enters the conduction band and electron-hole recombination occurs at the Eu^{2+} luminescence center.

Mather and Chakrabarti[18] et. al. examined the decay kinetics of the $MgS:Eu^{2+}:Sm^{3+}$ phosphor and concluded that electrons may also be optically detrapped from the Sm^{3+} traps by tunneling into an excited state of the Eu^{2+} luminescence center without entering the conduction band.

$$Sm^{2+} \rightarrow Sm^{3+} + e^{+}$$

$$Eu^{3+} + e^{\overset{-}{\cancel{+}}} \rightarrow Eu^{2+*}$$

$$Eu^{2+*} \rightarrow Eu^{2+} + h\nu$$

Chakrabarti et. al.[20] reported that the thermoluminescent emission spectra for the MgS:Eu:Sm phosphor is characteristic of Sm^{3+} rather than Eu^{2+}. Upon thermal stimulation, holes trapped at either a V^{-} center or at an Eu^{3+} ion will be released recombining with the trapped electron at the Sm atom.

$V^{-} \longrightarrow S^{-2} + V_{Mg} + e^{+}$

$Eu^{3+} \longrightarrow Eu^{2+} + e^{+}$

$Sm^{2+} + e^{+} \longrightarrow Sm^{3+*}$

$Sm^{3+*} \longrightarrow Sm^{3+} + h\nu$

D. Mechanisms for the Release of Trapped Electrons by Thermal or Optical Stimulation.

The configurational coordinate model[5] is a schematic diagram used to describe the relationships between different energy levels in space. The configurational coordinate r_o is shown in Figure 1 on the abscissa in units of length. This coordinate shows the relationship of energy levels in one dimension.

An electron in the trapping state with equilibrium energy U_1 and configurational coordinate r_1 is forbidden to spontaneously decay to the luminescence center by electrostatic forces from the atoms of the surrounding lattice. It may be thermally excited into the state of the conduction band by absorbing $E_{thermal} = kT$ quanta of energy and tunnel into the conduction band at point A, where it may radiatively decay to the luminescence center. This is known as thermoluminescence and is the principle behind the operation of most conventional personnel dosimeters.

The electron may also be optically excited by absorbing

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* - Indicates an excited state for the ion.

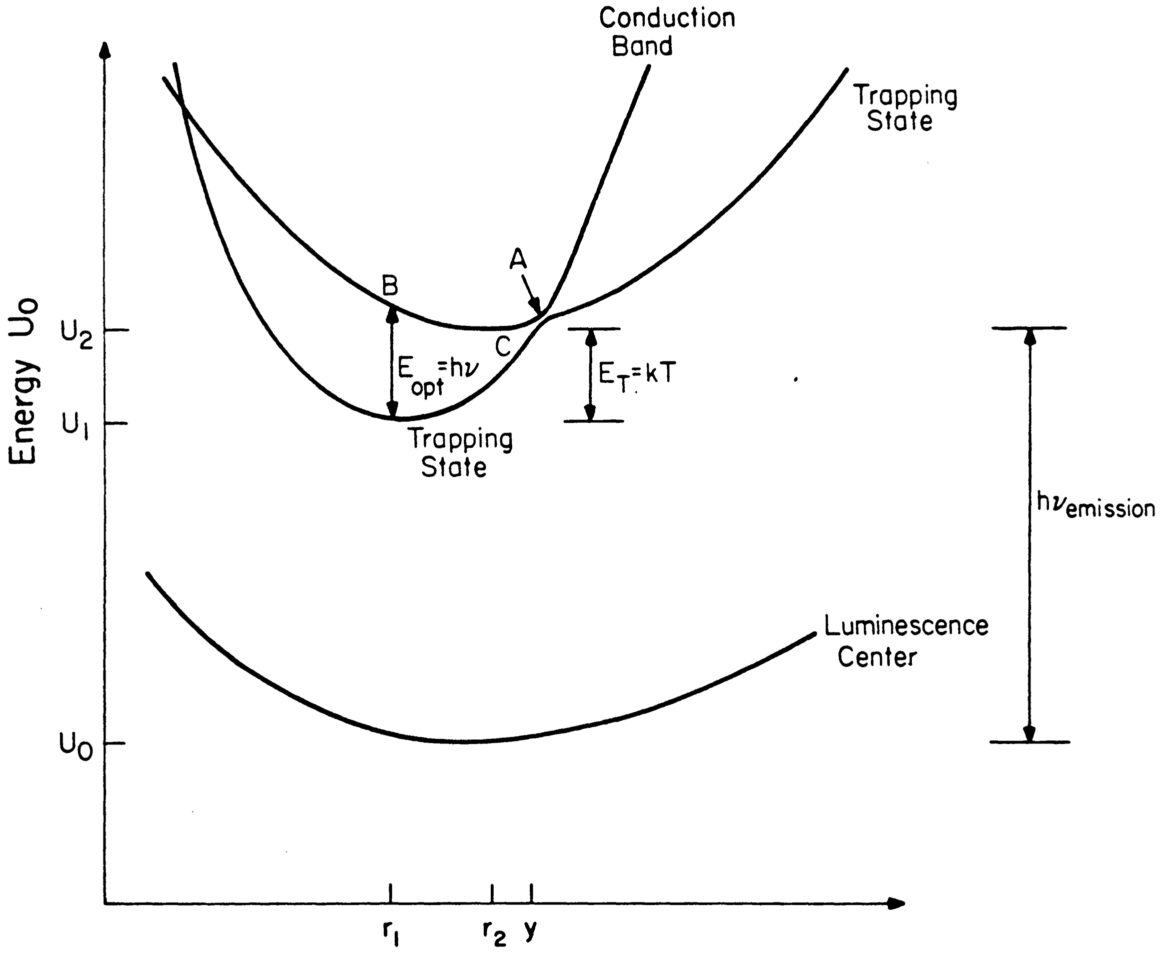

Figure 1. Schematic representation of phosphor energy levels in one dimension.

$E_{opt.} = h\nu$ quanta of photonic energy from the trapping state to B on the conduction band. It will non-radiatively decay to C at r_2 and radiatively decay while emitting $h\nu$ of photonic energy.[5] In most ionic crystals, r_1 and r_2 do not have the same configurational coordinate. Curie[5] stated that $E_{opt.} > E_{thermal}$ unless a direct band gap* exists between the two excited states.

E. Trapping Parameters.

Historically, empirical data obtained as thermoluminescence peaks were used to calculate the depth of electron traps. Thermoluminescence is characterized by peaks in intensity at a specific emission wavelength with temperature.

Randall and Wilkins[10] proposed a simple model for the trap depth.

$E = 21kT_m$ where k is Boltzmann's constant and T_m the maximum on the thermoluminescence emission peak.

More recent studies associate the trap depth with the shape of the thermoluminescent peak and kinetic data derived from the thermoluminescent decay.[3,27]

Trap depths suitable for dosimetry purposes have thermoluminescent maxima at no less than 473°K. Shallower

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*A material has a direct band gap if the lowest energy position of the conduction band and the highest energy position of the valence band have the same value of k in k space. GaAs is a material possessing a direct band gap.

trap depths may be emptied by ambient temperatures. MgS:Eu^{+2}:Sm^{+3} has a T_m peak at 533°K corresponding to a trap depth of 0.71 eV.[12]

F. Optically Stimulated Luminescence Dosimeters.

The phenomenon of optically stimulated luminescence was first suggested for use in personnel dosimetry by Antonov-Romanovski (1956)[1] who studied the infrared-stimulable SrS:Eu^{2+}:Sm^{3+}.

Sanborn and Beard[14] in 1967 studied Eu^{2+} and Sm^{3+} doped sulfides of strontium, calcium and magnesium. They concluded that MgS showed the most promise as a host lattice for OSL dosimeters because of its sensitivity to lower levels of radiation (10 millirads), its ease of stimulation by infrared light, its stability against spontaneous detrapping and its low effective atomic number ($Z_{eff.}$)

Rao[12] and others observed that the wavelength of optical stimulation for MgS:Eu^{2+}:Sm^{3+} is 1.07 μm which is close to the emission wavelength of YAG:Nd^{3+} crystal lasers. Samples were prepared, irradiated with gamma rays, and the traps emptied by the laser. Emission peak heights were compared to radiation dose and a linear correlation was observed.

Mathur et. al.[8] studied the OSL phosphor MgS:Ce^{3+} Sm^{3+} and observed that the tunneling mechanism of trapping and recombination is similar to that of MgS:Eu^{2+}, Sm^{3+}

phosphors. A comparison of the optical properties of the two materials is shown on Table 1.

G. Preparation of $(Mg_{1-x-y},Eu_x,Sm_y)S$

Sanborn and Beard[14] (1967) prepared $(Mg_{1-x-y},Eu_x,Sm_y)S$ by reducing $MgSO_4$ with argon bubbled through CS_2 at temperatures between 700-1000°C. The $MgSO_4$ was pre-doped with europium and samarium chlorides. A range of reducing temperatures were tried with the optimum phosphor sensitivity occurring at 800°C.

Asano and Nakao[2] produced $(Mg_{1-x},Eu_x)S$ by reducing purified $MgSO_4$ in a stream of N_2 and CS_2 at 750°C. With MgS prepared, EuF_3 was added and the mixture was heated at 1000°C for 40 min, in N_2 and H_2S.

Recently Yamashita and Asano[15] (1986) prepared Sm^{3+} doped magnesium sulfides by heating pre-doped $MgSO_4$ in N_2 + CS_2 at 1000°C for 40 min. The reduction process was described as,

$$3MgSO_4 + 4CS_2 \longrightarrow 3MgS + 4COS + 4SO_2$$

X-Ray diffraction results revealed that all of the sulfate had reacted.

Table 1. Comparison of the OSL properties of MgS:Ce^{3+}:Sm^{3+} with MgS:Eu^{2+}:Sm^{3+}.[8,12]

	Phosphor	
	MgS:Eu:Sm	MgS:Ce:Sm
T_{max} (^{o}K)	523	449
Wavelength of Stimulated Emission (nm)	589	520
Wavelength of OSL excitation (μm)	1.07	1.32
Mechanism of Trap Release	Ejection into conduction band or tunneling from an excited state of the trap to a luminescence center.	Ejection into conduction band or tunneling from an excited state of the trap to a luminescence center.

III. EXPERIMENTAL PROCEDURE

A. Sample Preparation.

The phosphors were prepared by blending selected oxides with 99.9% pure anhydrous $MgSO_4$. For a description of the raw materials used, refer to Appendix 1. The powders were blended in a beaker with a magnetic stirrer in acetone* at 100°C and then dried in a drying oven at 200°C for 1 hour to evaporate the remaining acetone.

B. Firing Procedure.

The samples were placed in 10-mL alumina combustion boats and two combustion boats were placed in a mullite tube and the ends were sealed with hard rubber stoppers. The samples were heated in an electrical resistance heated tube furnace in an atmosphere of Ar bubbled through carbon disulfide. The firing temperature was measured with a Type S thermocouple and selected by firing a series of samples at various temperatures and selecting the temperature producing the brightest UV emission. The samples were allowed to furnace cool in inert gas, then removed and washed in carbon disulfide to remove the excess sulfur. Finally, they were ground until all particles passed through a Standard 200-mesh sieve.

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*Acetone is used instead of water to prevent the anhydrous $MgSO_4$ from hydrating.

C. Luminescence Measurements.

Emission spectra of the phosphors were obtained using a Perkin Elmer LS-5B spectrophotometer, by exciting the sample with 250nm radiation and scanning from 280nm to 720nm. Excitation spectra were obtained by measuring the peak emission intensity as the exciting radiation changes from 230nm to the wavelength of the peak emission. An attenuator and low wavelength filter were used to reduce the signal and remove higher order reflections of the excitation wavelength.

Brightness measurements were obtained by measuring the intensity at the peak wavelength at room temperature under 250 nm excitation with a Perkin-Elmer LS-5B photomultiplier. The resolution on the monochromator was 2nm. The brightness values were compared to the brightness of the $(Mg_{.999},Eu_{.001},Sm_{0.001})S$ phosphor, which was assigned a value of 100.

D. Thermoluminescent Glow Curve Measurements*

Thermolumenscence Measurements were made using a Harshaw Model 2000B TL reader. Standard 200 mesh powders were deposited on 25 mm x 25 mm glass slides by sedimentation in ethanol and were exposed to ultraviolet radiation from a mercury lamp for one minute. They were

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*Measurements were performed at the Naval Surface Weapons Center in White Oak, Maryland.

tested at a heating rate of 5 K/sec and the TL curves were recorded upon an X-Y recorder.

E. OSL Measurements*

The spectral dependence and luminous intensity of OSL emissions were measured with an EG&G PARC optical multichannel analyzer with a silicon diode array cooled to-25^{0}C. The standard 200 mesh samples were deposited onto 25mm by 25mm glass slides in an ethanol slurry, pre-excited with UV light from a mercury lamp for one minute, and exposed to a 1.06 μm YAG:Nd^{3+} laser for optical stimulation. Each measurement was made at 300K.

F. OSL Stimulation Spectra*

Stimulation spectra of OSL were excited by monochromatic light from a standard tungsten lamp. The stimulated emission was detected by a 9658R EMI photomultiplier. A cut-off filter was placed between the monochromator and the sample to eliminate light of wavelengths below 700nm. The samples were prepared and irradated as described in section E.

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*Measurements were performed at the Naval Surface Warfare Center in White Oak, Maryland.

IV. EXPERIMENTAL RESULTS

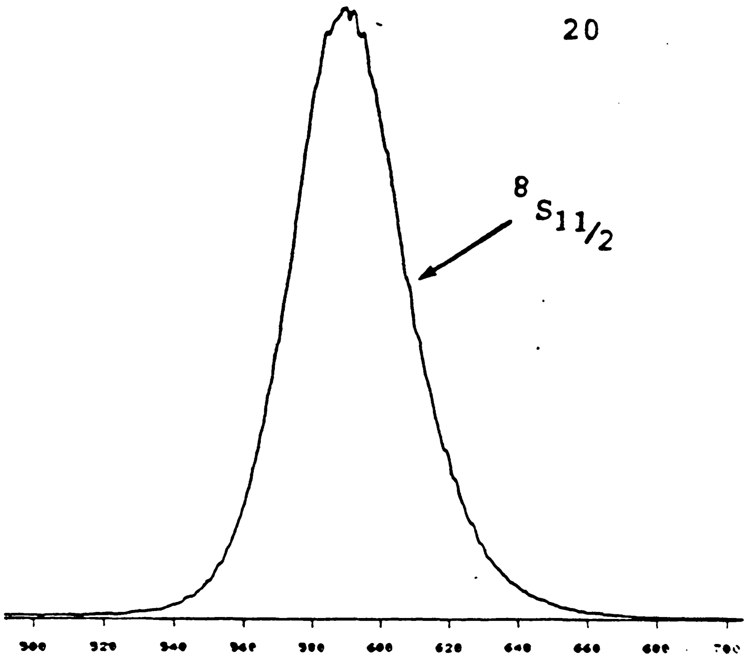
A. Optical Properties of the MgS:Eu^{2+},Sm^{2+} Concentration Series.

To determine the effect of activator concentration on luminescence, a series of sixteen samples was synthesized with the general composition $(Mg_{1-x-y},Eu^{2+}{}_x,Sm^{3+}{}_y)S$. Each sample was fired at 800°C, the optimum temperature reported in the literature.[14] The subscripts x and y have values of 0.0, 0.0001, 0.001 and 0.01 and each permutation was prepared. X-ray diffraction data revealed that all samples were MgS with the halite crystal structure.

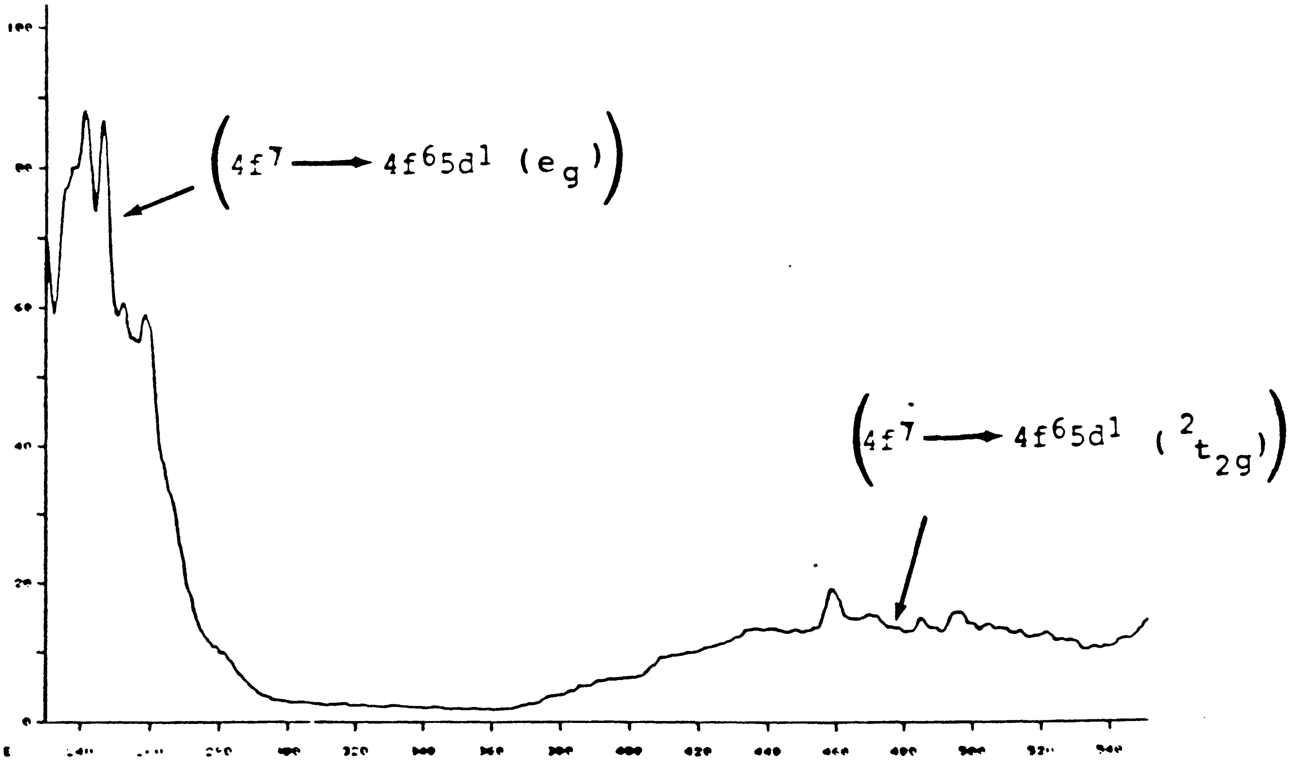
1. UV Excited Luminescence

The brightness, excitation spectra and emission spectra were measured for each sample in the series, and the spectral characteristics were compared with data from the literature.[2,9,15] The only observed excitation and emission lines were those corresponding to Eu^{2+} and Sm^{3+}. The excitation and emission spectra of singly activated MgS:Eu^{2+} and MgS:Sm^{3+} are shown in Figures 2 and 3 respectively. Luminescence data for the entire $(Mg_{1-x-y},Eu^{2+}{}_x,Sm^{3+}{}_y)S$ concentration series are shown in Table 3.

In several of the doubly activated samples, both the Eu^{2+} and Sm^{3+} emissions appear in the emission spectrum. Because the emission wavelengths of the most intense Sm^{3+}

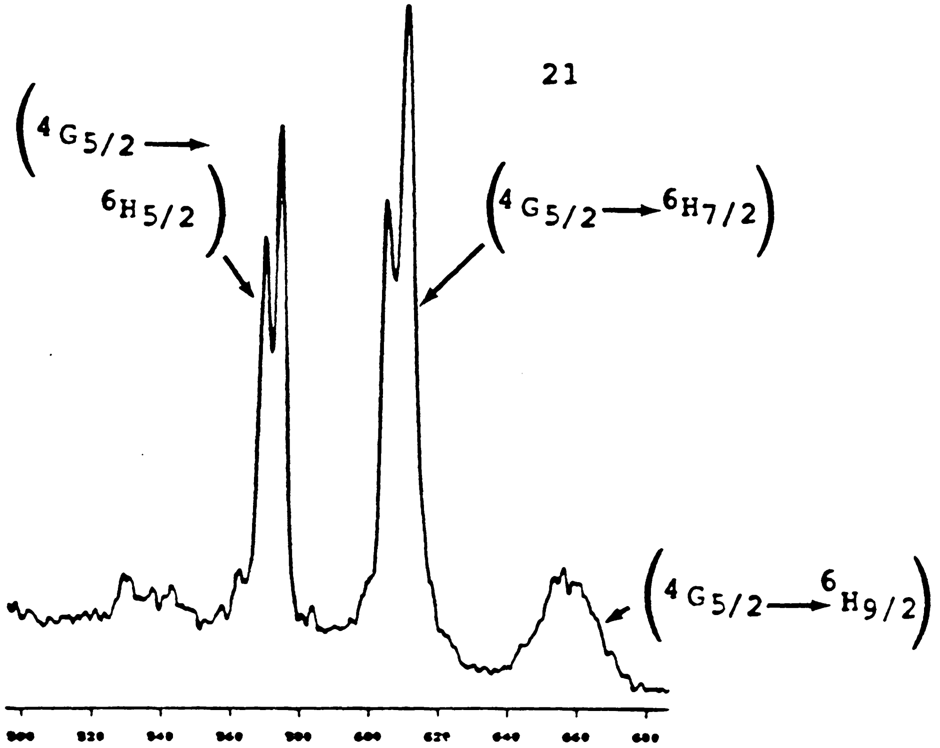


a.) Emission Spectra

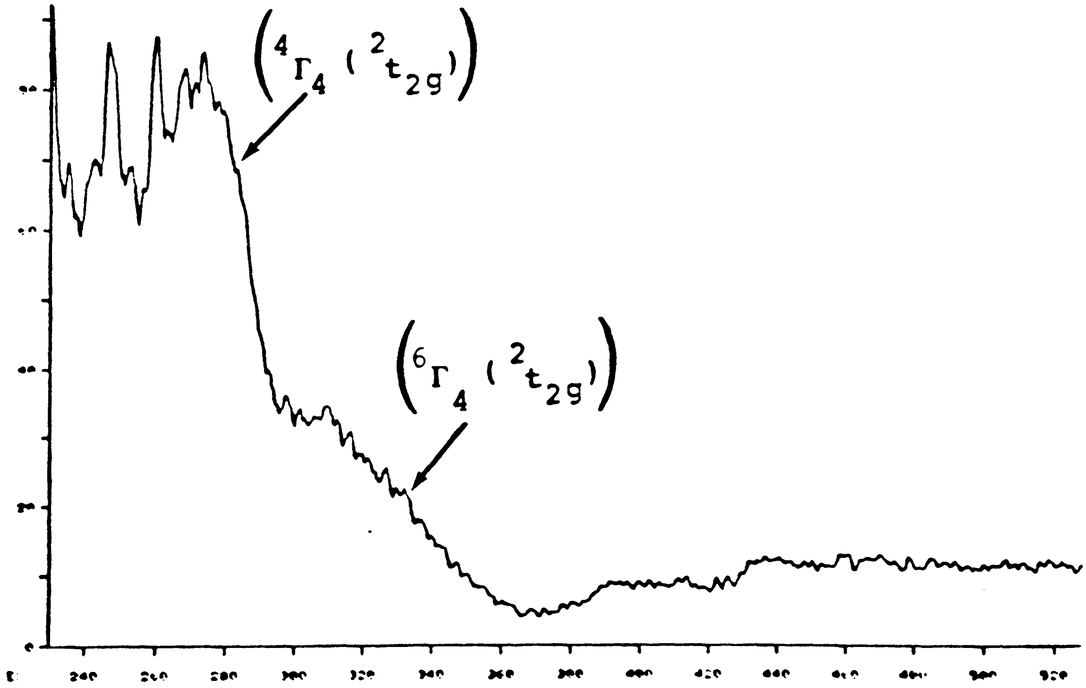


b.) Excitation Spectra

Figure 2. Excitation and emission spectra for the $(Mg_{0.999}, Eu^{2+}_{0.001})S$ phosphor.



a.) Emission Spectrum



b.) Excitation Spectrum

Figure 3. Excitation and emission spectra for the $(Mg_{0.999}, Sm^{3+}{}_{0.001})S$ phosphor.

Table 3. Luminescence Data for $(Mg_{1-x-y},Eu^{2+}_x,Sm^{3+}_y)S$ Phosphors under 250nm Excitation

Composition					
x	y	Body Color	Dominant Activator	Dominant Emission Wavelengths (nm)	Relative Emission Peak Height
0.0	0.0	White	not-luminescent	not-luminescent	---
0.0	0.0001	White	Sm^{3+}	610	3
0.0	0.001	Light Tan	Sm^{3+}	610	5
0.0	0.01	Red-Brown	Sm^{3+}	610	1
0.0001	0.0	White	Eu^{2+}	589	31
0.0001	0.0001	White	Eu^{2+}	589	6
0.0001	0.001	Light Tan	Eu^{2+}	589	4
			Sm^{3+}	610	4
0.0001	0.01	Red-Brown	Sm^{3+}	610	2
0.001	0.0	Light Tan	Eu^{2+}	589	56
0.001	0.0001	Light Tan	Eu^{2+}	589	100
0.001	0.001	Light Tan	Eu^{2+}	589	28
0.001	0.01	Red-Brown	Sm^{3+}	610	2
			Eu^{2+}	589	1
0.01	0.0	Gray	Eu^{2+}	589	69
0.01	0.0001	Gray	Eu^{2+}	589	90
0.01	0.001	Gray	Eu^{2+}	589	67
0.01	0.01	Dark Gray	Eu^{2+}	589	1
			Sm^{3+}	610	1

lines (573nm and 609nm) are very close to the emission wavelength of the Eu^{2+} band (589nm), it is difficult to detect the presence of the Sm^{3+} lines by inspection of the emission spectrum. However, the presence of the Sm^{3+} emission may be detected by searching for the $H_{9/2}$ emission lines at 657nm in the emission spectrum or by delaying the time between UV excitation and photodetection to observe the slow decaying Sm^{3+} 609 nm. emission line.

Figures 4 and 5 show the effect of activator concentration on the Eu^{2+} and Sm^{3+} emissions intensities respectively. The intensities expressed are relative to the intensity of the $(Mg_{0.9989}, Eu^{2+}_{0.001}, Sm^{3+}_{0.0001})S$ phosphor. The Eu^{2+} emission band predominates unless there is a high Sm^{3+} concentration (1.0 mole percent) as shown on Figure 6. The Eu^{2+} emission is an electric dipole induced (parity allowed) transition with a high transition probability, high intensity and short decay time, while the Sm^{3+} emission is an electric quadrapole induced (parity disallowed) transition with a low intensity, low probability and long decay time.

Figure 4 shows that low Sm^{3+} concentrations (<0.01 mole percent) will sensitize the Eu^{2+} emission band, while higher Sm^{3+} concentrations severely quench this emission. This sensitization effect is not observed for high Eu^{2+} concentrations (0.01 mole percent).

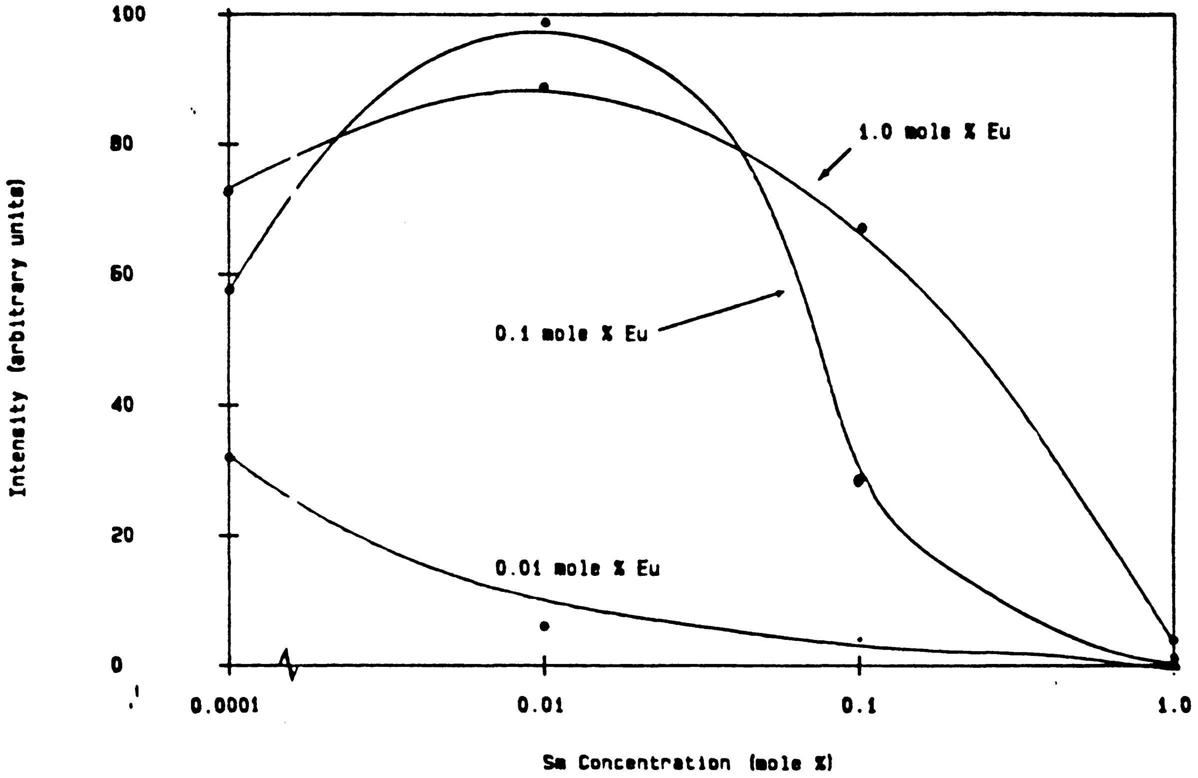


Figure 4. Effect of activator concentration on the UV(250nm) excited intensity of the 589nm Eu^{2+} emission band.

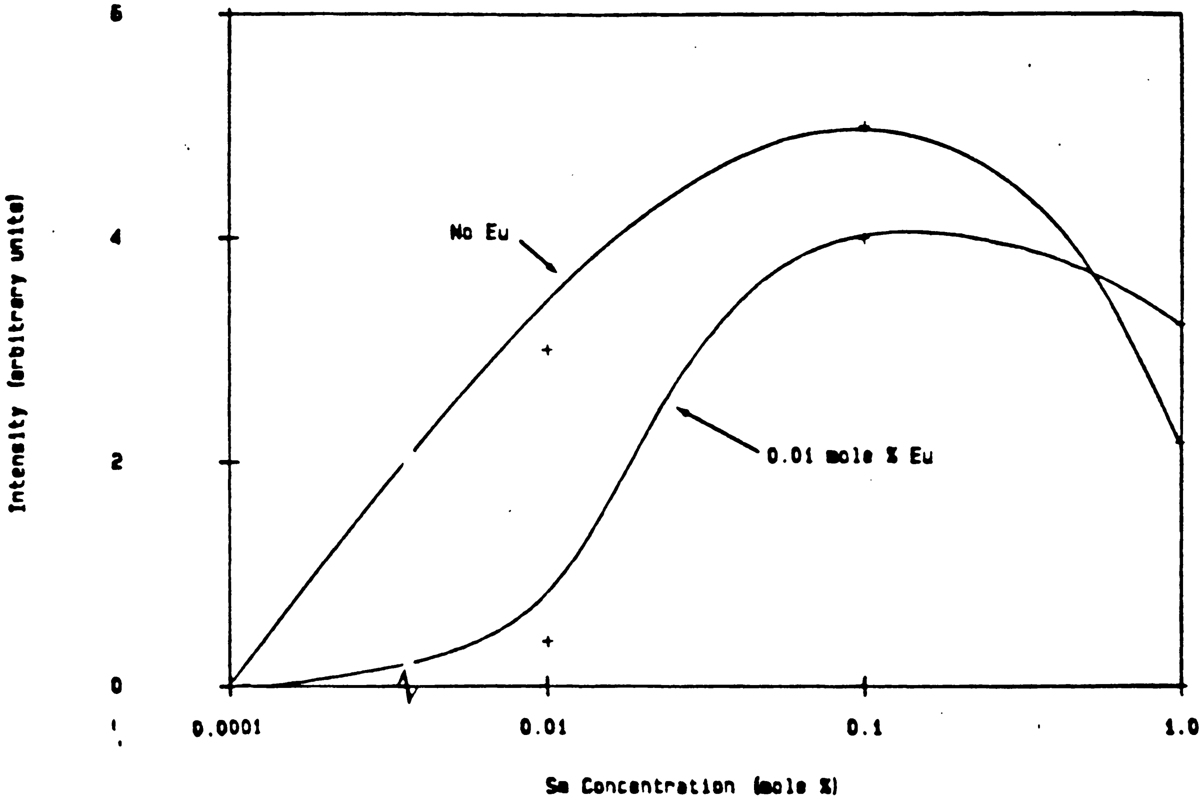


Figure 5. Effect of activator concentration on the UV (250nm) excited intensity of the 610nm Sm^{3+} emission band.

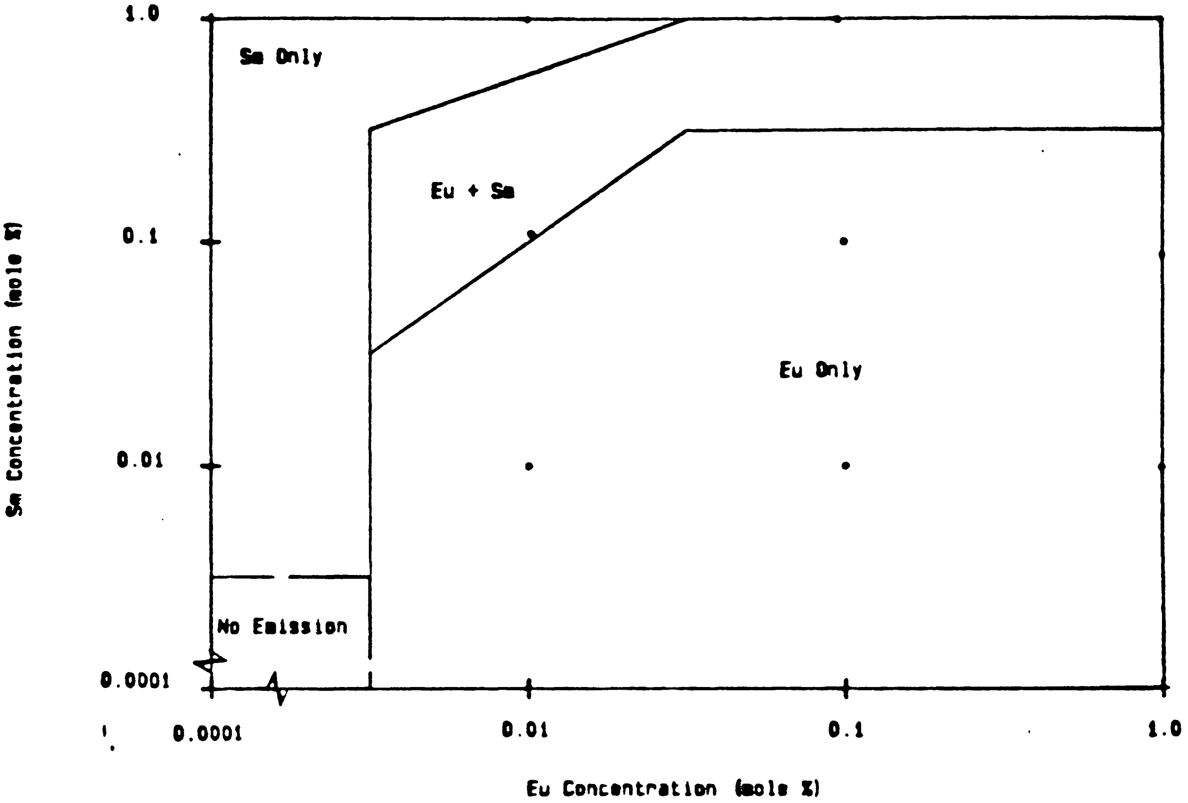


Figure 6. Regions of dominant activators under UV (250nm) excitation for the MgS:Eu^{2+}:Sm^{3+} series.

There is no spectral signature of Sm^{3+} in the excitation spectrum of the sensitized Eu^{2+} emissions, with the excitation spectra of the Eu^{2+} band and the Sm^{3+} lines identical to those of the singly activated material. The emission and excitation spectra for the entire concentration series is shown in Appendix 2.

2. UV Stimulated Thermoluminescence of $MgS{:}Eu^{2+},Sm^{3+}$.

Thermoluminescence (TL) data were taken for all of the doubly activated phosphors in the $(Mg_{1-x-y},Eu^{2+}{}_x,Sm^{3+}{}_y)S$ concentration series, with relative intensities listed in Table 4. All thermoluminescent glow curves are shown in Appendix 3.

The three thermoluminescent peaks prevalent in the samples studied were at 370, 395 and 662K. Figure 7 shows the dependence of peak brightness on activator concentration. The most intense thermoluminescent peaks occur at low concentrations (0.01 mole percent) of Eu^{2+} and Sm^{3+} with higher concentrations of both activators diminishing the peak brightnesses. In the samples containing 1 mole percent Eu^{2+}, regardless of the Sm^{3+} concentration, there is no evidence of the 662K peak, although a peak is observed beyond 673K, out of the range of the detector. It appears that high (1 mole percent) Eu^{2+} concentrations deepen the traps resulting in the high temperature TL peak in place of the 662K peak.

Table 4. Thermoluminescence data for $(Mg_{1-x-y},Eu_x,Sm_y)S$ phosphors

Composition		TL Peak Intensities (Relative Units)		
x	y	370°K	395°K	662°K
0.0	0.0001	13	--	--
0.0	0.001	7	6	--
0.0	0.01	4	--	--
0.0001	0.0	--	--	--
0.0001	0.00005	60	32	17
0.0001	0.0001	100	78	89
0.0001	0.001	9	71	18
0.0001	0.01	--	26	6
0.001	0.0	--	--	--
0.001	0.0001	15	--	21
0.001	0.001	16	--	14
0.001	0.01	3	--	--
0.01	0.0	--	--	--
0.01	0.0001	8	--	7
0.01	0.001	13	--	3
0.01	0.01	11	--	--

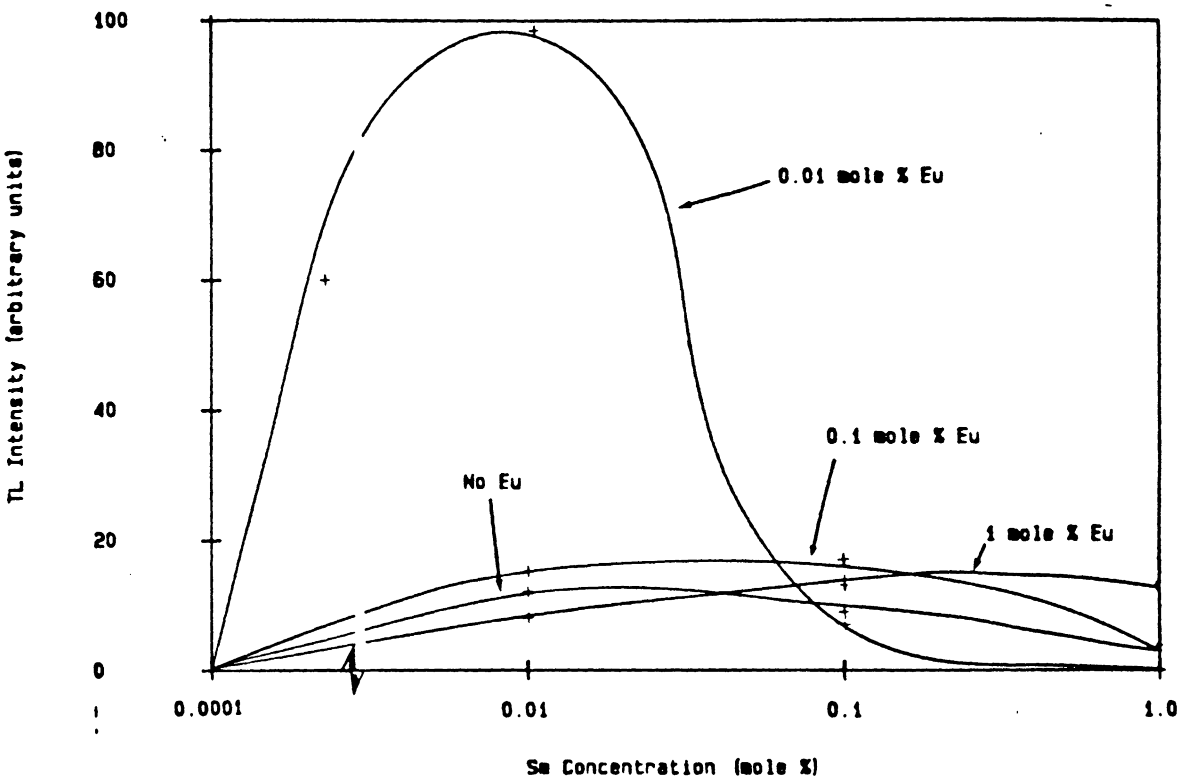


Figure 7a. Effects of Eu^{2+} and Sm^{3+} concentration on the intensity of the 370K thermoluminescent peak.

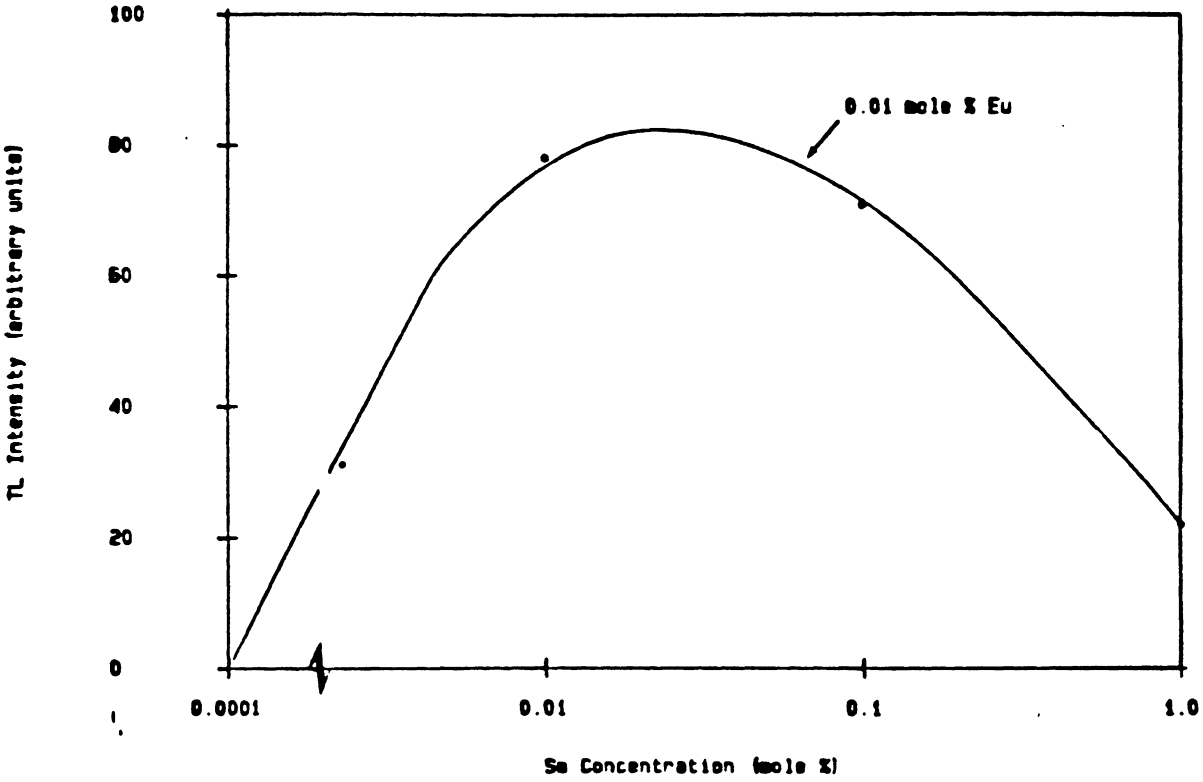


Figure 7b. Effect of Sm^{3+} concentration on the intensity of the 395K thermoluminescent peak.

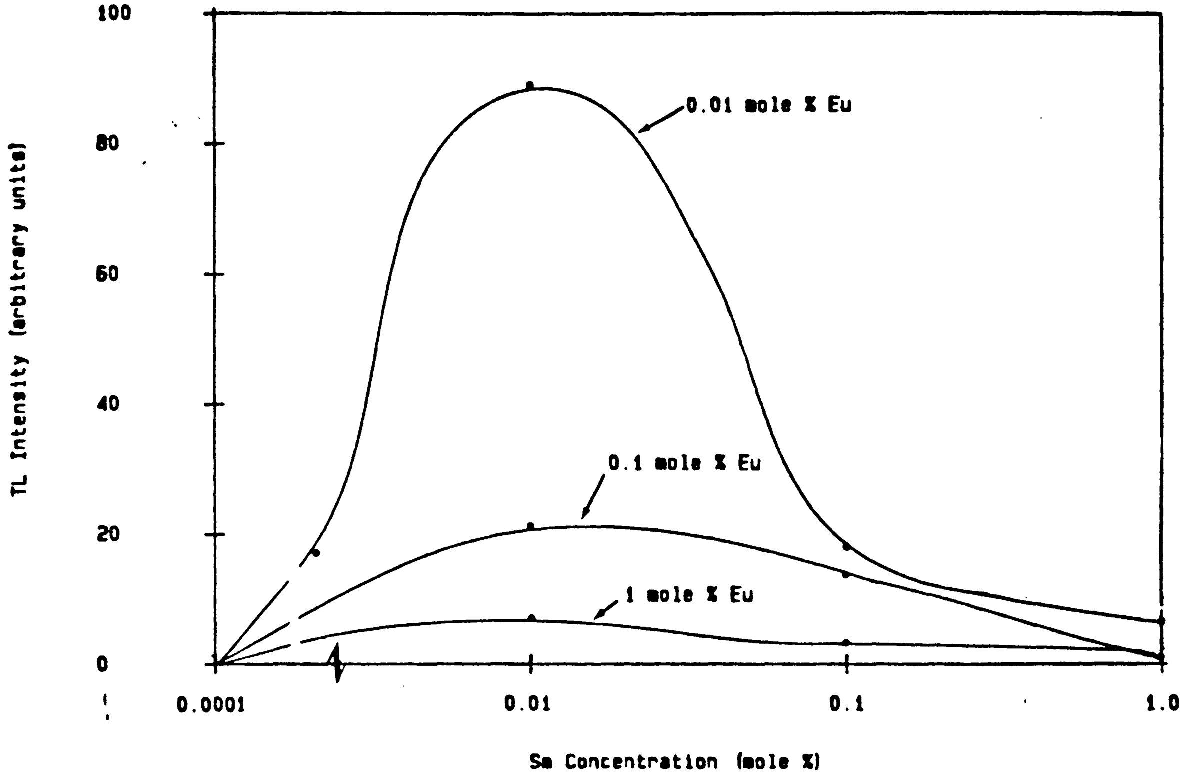


Figure 7c. Effect of Eu^{2+} and Sm^{3+} concentration on the intensity of the 662K thermoluminescent peak.

3. Optically Stimulated Luminescence of MgS:$Eu^{2+}Sm^{3+}$ Phosphors.

The sensitivity of the doubly activated $(Mg^{2+}{}_{1-x-y}, Eu^{2+}{}_x, Sm^{3+}{}_y)S$ phosphors to 1.06 μm optical stimulation after 1 min ultraviolet pre-excitation was examined, and in all of the samples showing OSL, the 589nm Eu^{2+} emission peak was observed as previously reported in the literature.[12] Figure 8 shows the relative OSL intensity after 1 min ultraviolet pre-excitation for all of the samples exhibiting optically stimulated luminescence. All optically stimulated emission peaks are exhibited in Appendix 3.

The sample containing 1.0 mole percent Eu^{2+} and 0.01 mole percent Sm^{3+} exhibited very weak OSL after ultraviolet pre-excitation and it is possible that with the high ratio of Eu^{2+} recombination centers to Sm^{3+} trapping centers that an electrons trapped will be able to tunnel to the recombination center without needing optical stimulation.

The optically stimulated intensity is greatest in the phosphors containing 0.1 mole percent Eu^{2+} and either 1.0 or 0.1 mole percent Sm^{3+} as shown in Figure 8. The samples with the optimum OSL intensity are not those with the optimum TL intensity.

The stimulation spectra for the optically stimulated emission consists of a broad band centered at 1.06μm, which is consistent with literature values for both the MgS:Eu^{2+}:Sm^{3+} and MgS:Ce^{3+}:Sm^{3+} phosphor systems.[8,12]

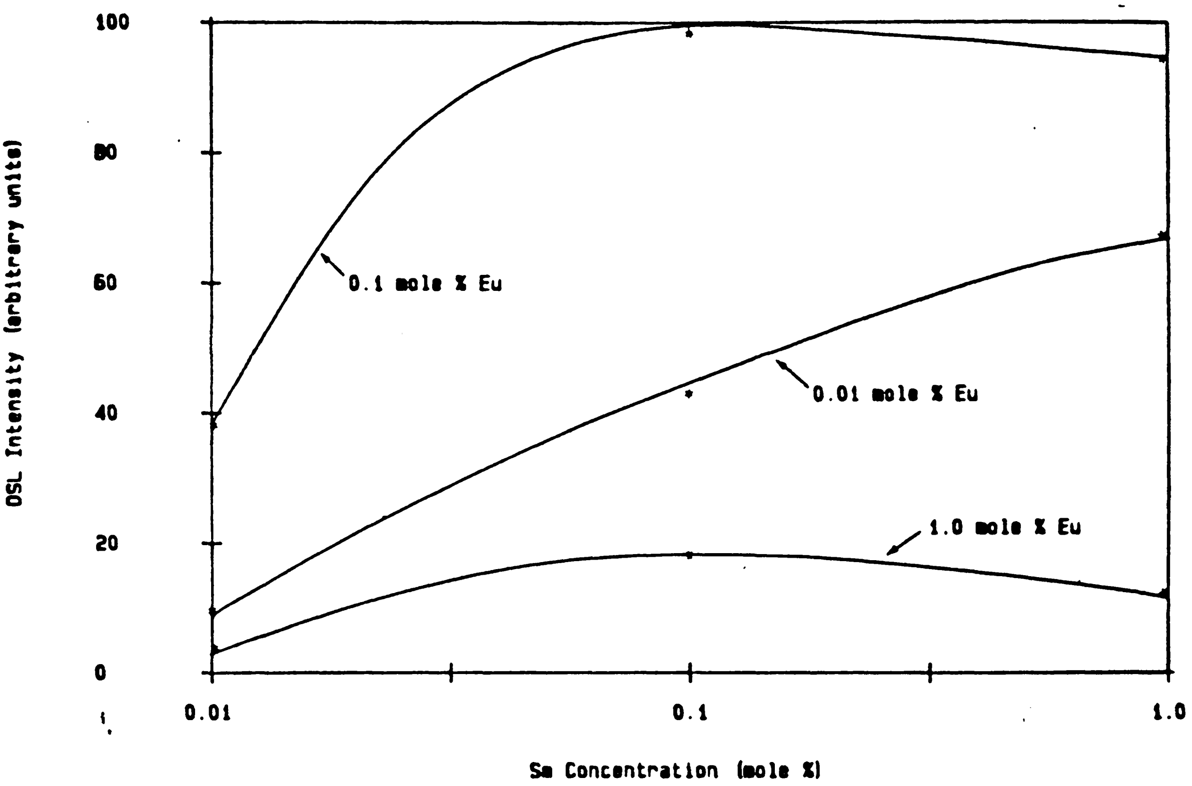


Figure 8. Relative YAG:Nd^{3+} laser stimulated OSL intensity of the $(Mg_{1-x-y},Eu_x,Sm_y)S$ series after 1 minute ultraviolet pre-excitation.

B. Effect of Cl^- Additions on the Optical Properties of the $MgS:Eu^{2+}:Sm^{3+}$ Phosphor.

It has been reported that the presence of Cl^- as a co-activator is important in enhancing the brightness of many alkaline earth sulfide phosphors.[7,11,23] Although the role of Cl^- additions is poorly understood, many CaS, SrS and BaS- based phosphors require its presence to luminescent.

Anhydrous $MgCl_2$ was added to the $(Mg_{0.998}, Eu^{2+}{}_{0.001}, Sm^{3+}{}_{0.001})S$ phosphor in concentrations of 0.005, 0.05 and 0.5 mole percent. X-ray diffraction data revealed no free $MgCl_2$ in any of the samples.

The addition of Cl^- considerably decreases the ultra-violet excited brightness of the 589nm peak of the $(Mg_{0.998}, Eu^{2+}{}_{0.001}, Sm^{3+}{}_{0.001})S$ phosphor with higher Cl^- concentrations having the greatest quenching effect. Figure 9 illustrates the effect of Cl^- concentration on the ultra-violet excited brightness of the $(Mg_{0.998}, Eu^{2+}{}_{0.001}, Sm^{3+}{}_{0.001})S$ phosphor. At a Cl^- concentration of 1 mole percent, both excitation bands are broadened, with the 480nm excitation band extending from 380nm to 660nm. The excitation and emission spectra are shown in Appendix 2.

Thermoluminescence tests of the $(Mg_{0.998}, Eu^{2+}{}_{0.001}, Sm^{3+}{}_{0.001})S$ phosphor with 0.1 mole percent Cl^- reveal a large peak at 573K near the value reported by Rao.[12] Figure 10 shows the TL Curve for the chlorinated phosphor pre-excited for 1 minute by ultraviolet excitation.

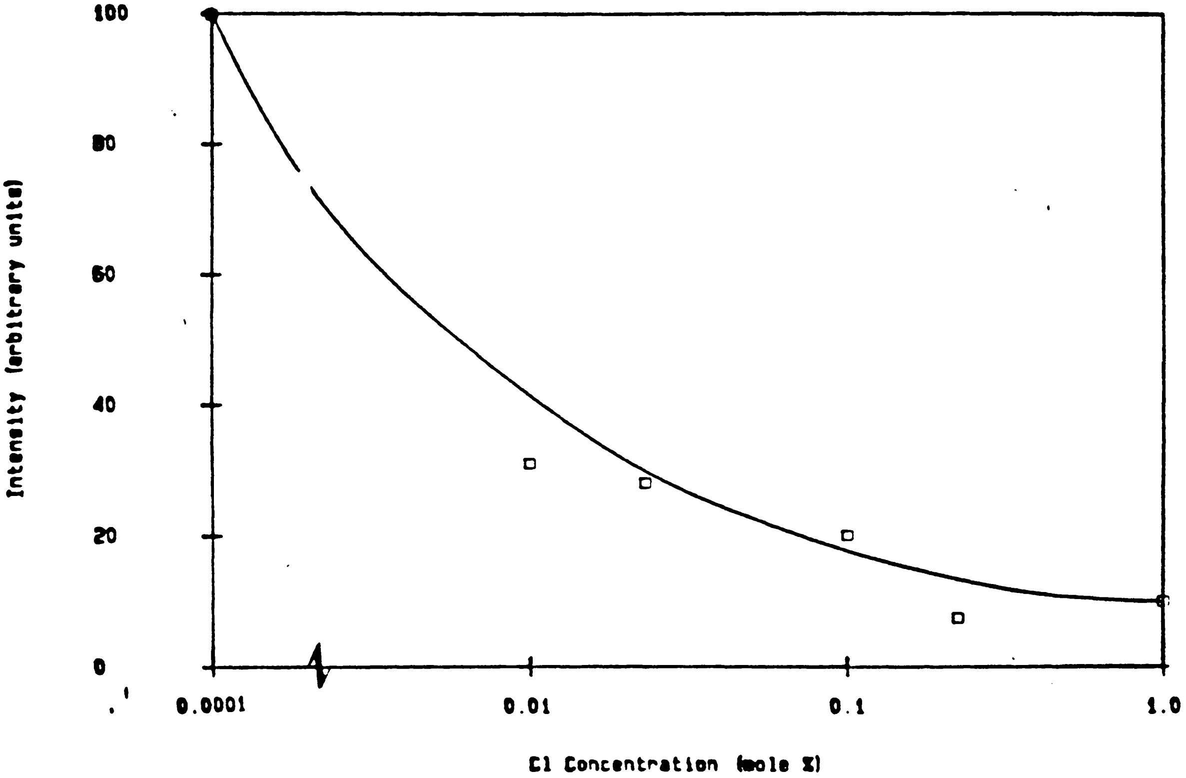


Figure 9. The effect of Cl^- concentration on the ultraviolet (250nm) brightness of $(Mg_{0.998},Eu_{0.001},Sm_{0.001})S$.

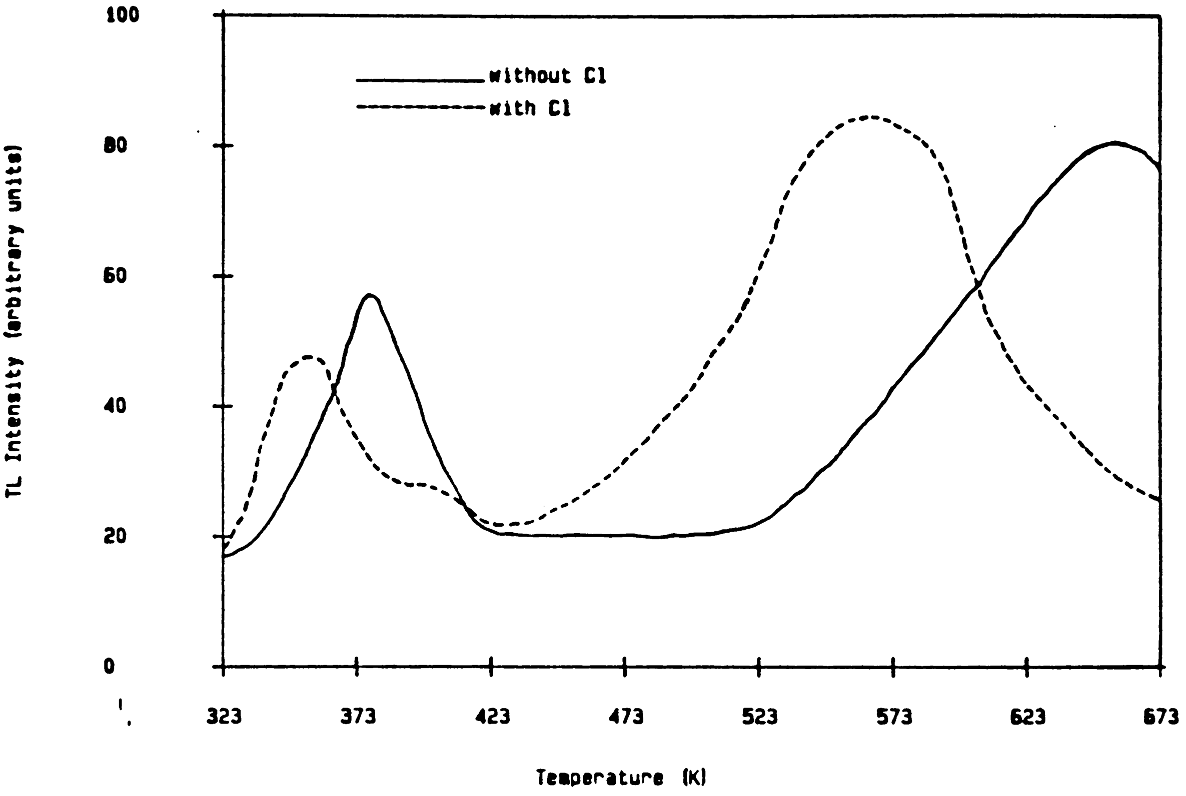


Figure 10. Thermoluminescences curves for $(Mg_{0.998},Eu^{2+}_{0.001},Sm^{3+}_{0.001})S$ phosphors with and without 0.1 mole percent $MgCl_2$ after 1 min. UV pre-excitation.

Additions of 0.1 mole percent Cl^- to the $(Mg_{0.998}, Eu^{2+}_{0.001}, Sm^{3+}_{0.001})S$ phosphor diminishes the intensity of the optically stimulated 589nm Eu^{2+} peak by 52%. The optically stimulated excitation spectra reveal that the peak wavelength of stimulation is shifted from 1.06 μm to 820nm (Figure 11).

D. Effect of d^{10}Activators on the Optical Properties of $MgS:Eu^{2+}:Sm^{3+}$ Phosphors.

It is desirable that the OSL emission wavelength be in the range of 500 — 550nm where the photodetector is most sensitive. With this in mind, a number of activators were added to the $(Mg_{0.998}, Eu^{2+}_{0.001}, Sm^{3+}_{0.001})S$ phosphor in concentrations of 0.01 and 0.1 mole percent in order to attempt to change the OSL emission wavelength.

The activators selected are parity-odd band-emitters*, like Eu^{2+}, where the primary electronic transitions are between a filled or partly filled $nd^{10}(n+1)s^2$ shell and an empty $(n+1)p$ shell. The activators examined included Cu^+, Ag^+, Sn^{2+}, Sb^{3+}, Pb^{2+} and Bi^{3+}. These particular activators were selected because their electronic properties are similar to Eu^{2+} and because each is a known activator in CaS with emission band peak at wavelengths lower than 589nm.[9]

The addition of 0.1 mole percent $Cu^+(3d^{10}4s^1)$ and $Ag^+(4d^{10}5s^1)$ to the $(Mg_{0.998}, Eu^{2+}_{0.001}, Sm^{3+}_{0.001})S$ phosphor, poisons both the ultraviolet stimulated and the

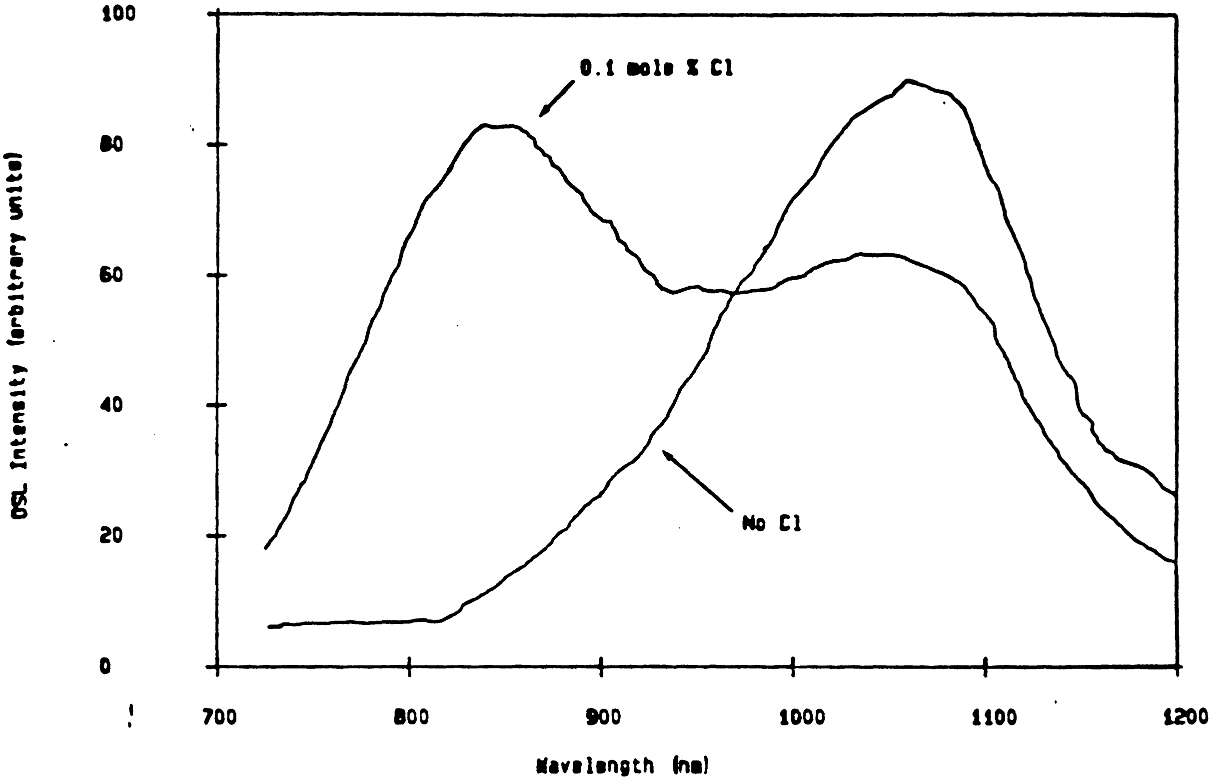


Figure 11. Effect of 0.1 mole percent Cl^- on the optical stimulation spectrum of the $(Mg_{0.998},Eu^{2+}_{0.001},Sm^{3+}_{0.001})S$ phosphor.

optically stimulated luminescence of the phosphor. Further research with Cu^{+} and Ag^{+} additions was not pursued.

The cations Sb^{3+} and Sn^{2+} are isoelectronic with the electronic configuration $[Kr]4d^{10}5s^{2}$, while Bi^{3+} and Pb^{2+} are isoelectronic with the electronic configuration $[Xe]5d^{10}6s^{2}$. The $MgS:Eu^{2+},Sm^{3+}$ phosphor with the addition of 0.1 mole percent Sb^{3+} or Sn^{2+} showed OSL, while the phosphor with equal amounts of Bi^{3+} or Pb^{2+} did not show synthesized in order to identify specific Sb^{3+}/Sn^{2+} excitation and emission peaks in $MgS:Eu^{2+}$, Sm^{3+}, Sb^{3+} and $MgS:Eu^{2+}$, Sm^{3+}, Sn^{2+} phosphors. The singly activated samples were preapred at $800^{\circ}C$ with an Sb^{3+}/Sn^{2+} concentration of 0.1 mole percent. The emission and excitation bands for the $MgS:Sb^{3+}$ and $MgS:Sn^{2+}$ phosphors are shown on Figures 12 and 13 respectively.

MgS activated with 0.1 mole percent Sb^{3+} produces a green emission band centered at 535nm and extending from 420 OSL. The effects of Sb^{3+} and Sn^{2+} were investigated further.

1. Characteristic UV Emission and Excitation Spectra of Singly Activated $MgS:Sb^{3+}$ and $MgS:Sn^{2+}$.

Samples of MgS singly activated with Sb^{3+}/Sn^{2+} were

*parity odd indicates an excited electron state with a charge in the orbital quantum number Δl of ± 1. This is Leporte's selection rule for allowed transitions. $4f \rightarrow 5d$ transitions have a Δl of -1 whereas $4f \rightarrow 4f$ transitions have a Δl of 0.

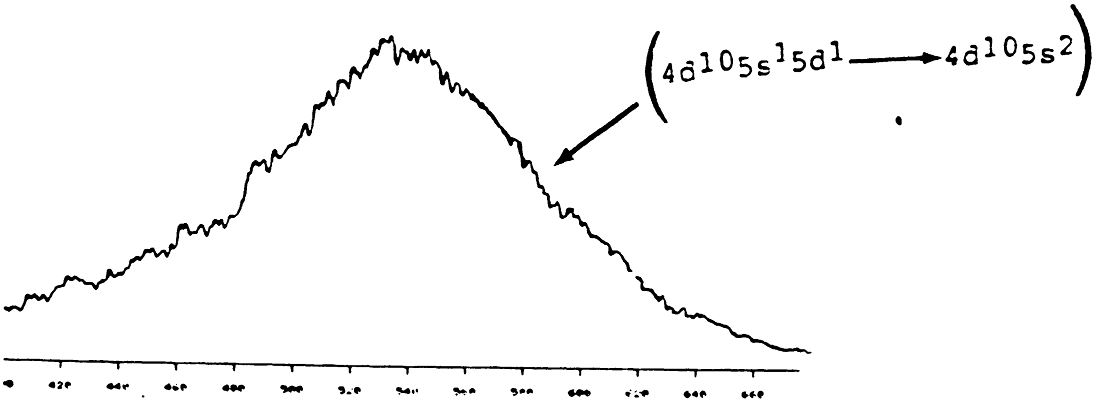
synthesized in order to identify specific Sb^{3+}/Sn^{2+} excitation and emission peaks in $MgS:Eu^{2+}$, Sm^{3+}, Sb^{3+} and $MgS:Eu^{2+}$, Sm^{3+}, Sn^{2+} phosphors. The singly activated samples were prepared at 800°C with an Sb^{3+}/Sn^{2+} concentration of 0.1 mole percent. The emission and excitation bands for the $MgS:Sb^{3+}$ and $MgS:Sn^{2+}$ phosphors are shown on Figures 12 and 13 respectively.

MgS activated with 0.1 mole percent Sb^{3+} produces a green emission band centered at 535nm and extending from 420 to 680nm. The strongest excitation band for $MgS:Sb^{3+}$ is at 340nm with weaker bands at 410, 373 and 260nm.

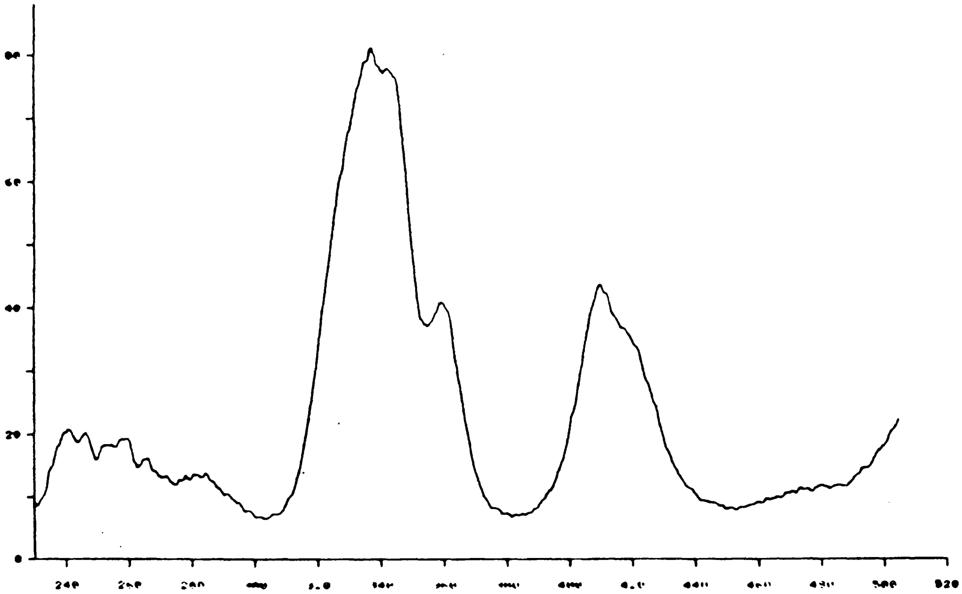
MgS activated with 0.1 mole percent Sn^{2+} possesses emission and excitation spectra similar to the $MgS:Sb^{3+}$ phosphor, although the emission intensity of the former is only 3% of that of the latter. Lehmann[7] reported that Sb^{3+} and Sn^{2+} have similar emission and excitation characteristics in the CaS host lattice. No attempt was made to enhance the emission brightness of either phosphor with a co-activator such as Cl^-.

2. UV Excited Emission and Excitation of Doubly Activated MgS Phosphors.

In order to observe optical interactions between activators in MgS phosphors, a number of doubly activated phosphors were synthesized. Table 5 lists the compositions, characteristic emission bands, and relative brightnesses for

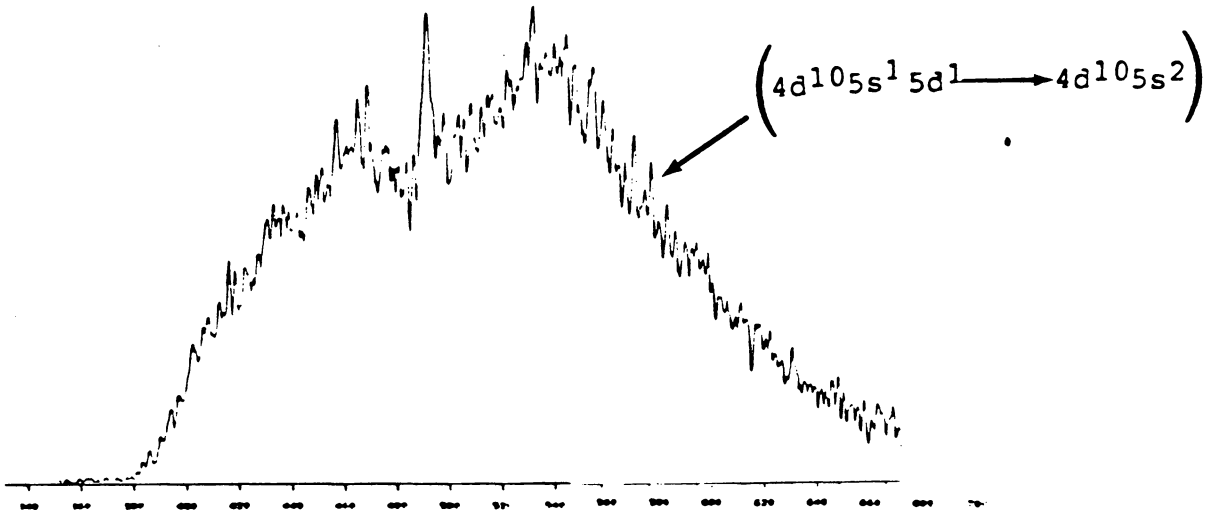


a.) Emission Spectra

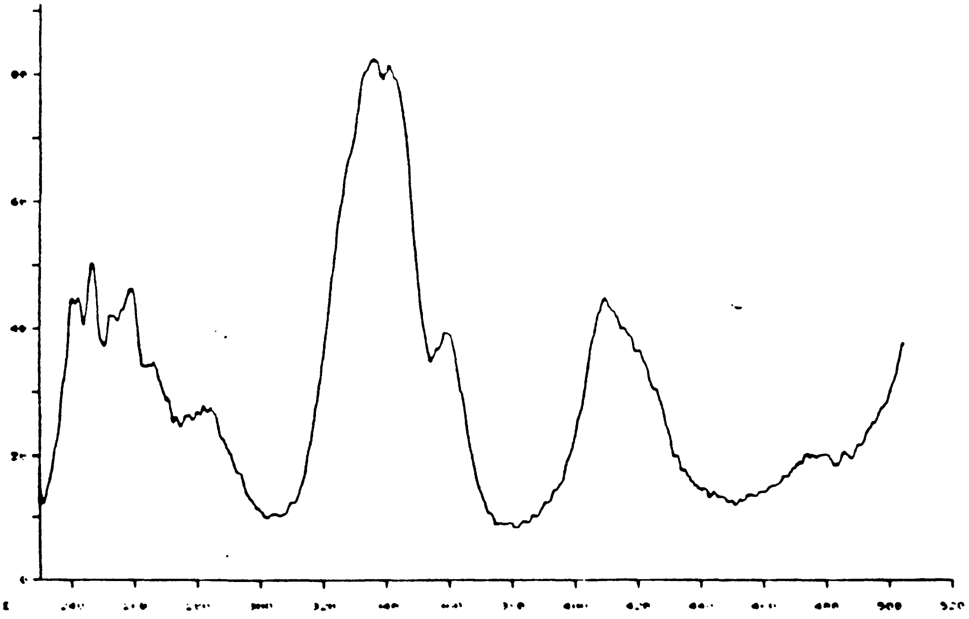


b.) Excitation Spectra

Figure 12. Excitation and emission spectra of the ($Mg_{0.998}$, $Sb^{3+}_{0.001}$)S phosphor



a.) Emission Spectra



b.) Excitation Spectra

Figure 13. Excitation and emission spectra of the $(Mg_{0.999}, Sn^{2+}_{0.001})S$ phosphor

Table 5. Ultraviolet-Excited Luminescence Data for Doubly-Activated MgS Phosphors.

Composition	Ultraviolet Excited Emission Wavelength (nm)	Intensity
$(Mg_{0.998},Eu^{2+}_{0.001},Sn^{2+}_{0.001})S$	Eu^{2+} (589nm)	100
	Sn^{2+} (535nm)	12
$(Mg_{0.998},Eu^{2+}_{0.001},Sb^{3+}_{0.001})S$	Eu^{2+} (589nm)	93
	Sb^{3+} (535nm)	21
$(Mg_{0.998},Sm^{3+}_{0.001},Sn^{2+}_{0.001})S$	Sm^{3+} (609nm)	1
	Sn^{2+} (535nm)	-
$(Mg_{0.998},Sm^{3+}_{0.001},Sb^{3+}_{0.001})S$	Sm^{3+} (609nm)	1
	Sb^{3+} (535nm)	-
Standard		
$(Mg_{0.998},Eu^{2+}_{0.001},Sm^{3+}_{0.001})S$	Eu^{2+} (589nm)	82

the materials investigated.

An indication of energy transfer from activator A to activator B is the presence of characteristic A excitation bands in the excitation spectra of the B activator. The excitation spectra for each observed emission band was examined for evidence of the other activator. The only indication of energy transfer from one activator to another is the presence of a small excitation peak at 460nm, characteristic of Eu^{2+} in the 535nm (Sb^{3+} or Sn^{2+}) excitation spectra of the $MgS:Eu^{2+}:Sn^{2+}$ and $MgS:Eu^{2+}:Sb^{3+}$ phosphors. It is uncertain whether the presence of characteristic excitation peaks for the Sb^{3+} or Sn^{2+} emissions in the excitation spectra of the Eu^{2+} (589nm) is due to energy transfer or to the overlap of the broad emission band of the $4d^{10}$ activators with the emission bands of Eu^{2+} and Sm^{3+}.

3. UV Excited Emission and Excitation of Triply-Activated MgS Phosphors.

A series of six samples were synthesized with the general formula $(Mg_{0.998-x},Eu^{2+}{}_{0.001},Sm^{3+}{}_{0.001}[A]_x)S$ with A = Sn^{2+} or Sb^{3+} and x = 0.0001, 0.001 or 0.01. All were fired at 800°C in argon bubbled through CS_2.

For the $MgS:Eu^{2+},Sm^{3+}$ phosphors containing variable Sb^{3+} concentration, the Eu^{2+} peak is prominent in all samples. The Sb^{3+} peak only appears in the sample with x =

0.0001 and it is only 11% of the peak brightness of the Eu^{2+} peak, while higher Sb^{3+} concentrations quench out the Sb^{3+} peak. The excitation spectra from the 589nm peak is identical to that of the singly doped $MgS:Eu^{2+}$ phosphor.

In the concentration series containing Sn^{2+}, there is no evidence of Sn^{2+} in the emission or excitation spectra of the phosphor. The effects of Sb^{3+} and Sn^{2+} on the brightness of each characteristic emission are shown on Figure 14.

4. Optically Stimulated Luminescence of Phosphors Containing d^{10} Activators.

All of the samples containing Sb^{3+} or Sn^{2+}, with the exception of those singly activated, showed optically stimulated luminescence when exposed to 1.06 μm infrared light after one minute of ultraviolet pre-excitation. Table 6 lists each phosphor, characteristic OSL peaks and OSL intensities.

The two samples containing Eu^{2+} and either Sn^{2+} or Sb^{3+} both exhibited the 589nm Eu^{2+} emission peak and the 535nm emission peak of Sn^{2+} or Sb^{3+} under 1.06 μm wavelength stimulation. In both cases the 589nm Eu^{2+} emission peak was dominant.

The two activator samples containing Sm^{3+} and either Sn^{2+} or Sb^{3+} showed the intense Sm^{3+} lines under optical stimulation, with no indication of the 535nm emission of

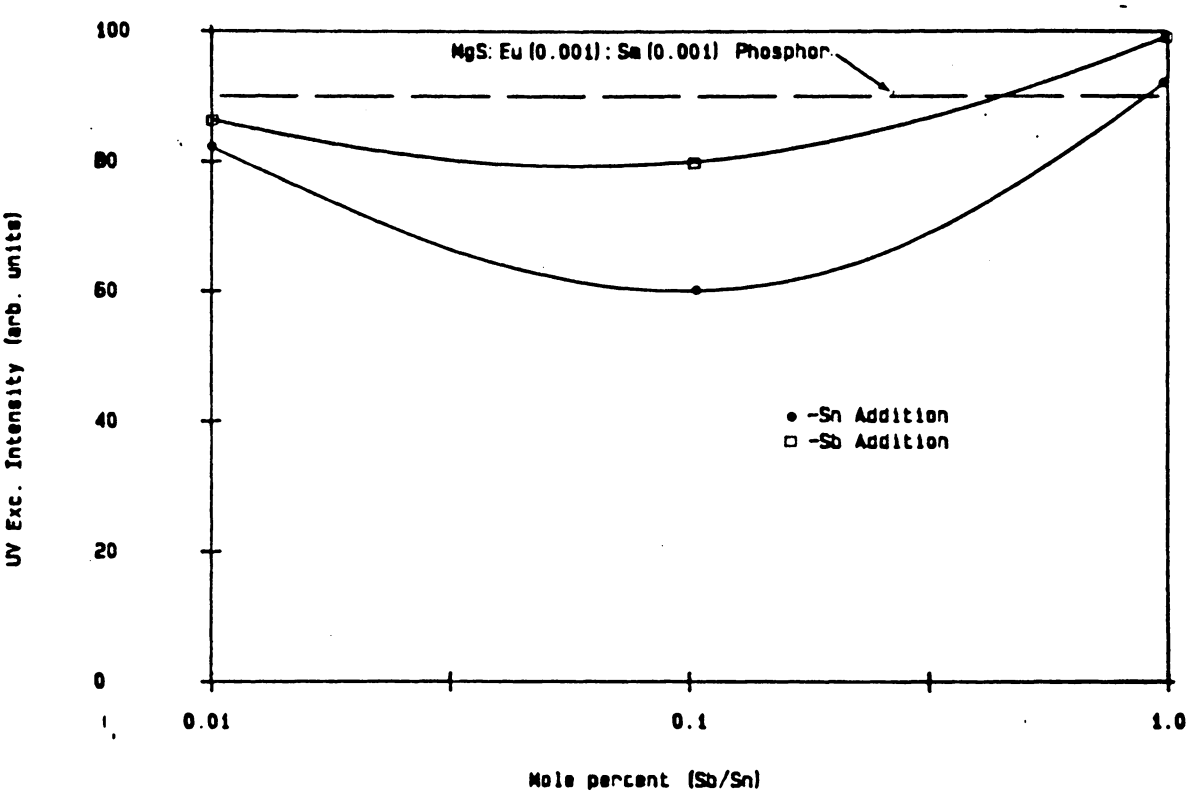


Figure 14. Effect of Sn^{2+} and Sb^{3+} on the UV (250nm) excited brightness of the Eu^{2+} emission of the $(Mg_{0.998},Eu^{2+}_{0.001},Sm^{3+}_{0.001})S$ phosphor.

Table 6. Characteristic OSL emission Intensities for MgS Phosphors containing d^{10} Activators.

Phosphor Composition	Characteristic OSL Emission	Relative Intensity
Standard		
$(Mg0.998, Eu^{2+}0.001, Sm^{3+}0.001)S$	Eu^{2+}(589nm)	52
Transition Group I - Three Activators		
$(Mg0.9979, Eu^{2+}0.001, Sm^{3+}0.001, Cu^{+}0.0001)S$	none	---
$(Mg0.997, Eu^{2+}0.001, Sm^{3+}0.001, Cu^{+}0.001)S$	none	---
$(Mg0.9979, Eu^{2+}0.001, Sm^{3+}0.001, Ag^{+}0.0001)S$	none	---
$(Mg0.997, Eu^{2+}0.001, Sm^{3+}0.001, Ag^{+}0.001)S$	none	---
$4d^{10}$ Two Activators		
$(Mg0.998, Eu^{2+}0.001, Sn^{2+}0.001)S$	Eu^{2+}(589nm)	11
	Sn^{2+}(535nm)	5
$(Mg0.998, Eu^{2+}0.001, Sb^{3+}0.001)S$	Eu^{2+}(589nm)	13
	Sb^{3+}(535nm)	7
$(Mg0.998, Sm^{3+}0.001, Sn^{2+}0.001)S$	Sm^{3+}(609nm)	92
$(Mg0.998, Sm^{3+}0.001, Sb^{3+}0.001)S$	Sm^{3+}(609nm)	100
$4d^{10}$ Three Activators		
$(Mg0.9979, Eu^{2+}0.001, Sm^{3+}0.001, Sn^{2+}0.0001)S$	Eu^{2+}(589nm)	16
	Sn^{2+}(535nm)	4
$(Mg0.997, Eu^{2+}0.001, Sm^{3+}0.001, Sn^{2+}0.001)S$	Eu^{2+}(589nm)	9
	Sn^{2+}(535nm)	2
$(Mg0.988, Eu^{2+}0.001, Sm^{3+}0.001, Sn^{2+}0.001)S$	Eu^{2+}(589nm)	7
	Sn^{2+}(535nm)	2
$(Mg0.9979, Eu^{2+}0.001, Sm^{3+}0.001, Sb^{3+}0.0001)S$	Eu^{2+}(589nm)	36
	Sb^{3+}(535nm)	25
$(Mg0.997, Eu^{2+}0.001, Sm^{3+}0.001, Sb^{3+}0.001)S$	Eu^{2+}(589nm)	25
	Sb^{3+}(535nm)	15
$(Mg0.988, Eu^{2+}0.001, Sm^{3+}0.001, Sb^{3+}0.01)S$	Eu^{2+}(589nm)	7
	Sb^{3+}(535nm)	11
$5d^{10}$ Three Activators		
$(Mg0.997, Eu^{2+}0.001, Sm^{3+}0.001, Pb^{2+}0.001)S$	none	---
$(Mg0.997, Eu^{2+}0.001, Sm^{3+}0.001, Bi^{3+}0.001)S$	none	---

Sb^{3+} or Sn^{2+} in either sample. This is an interesting result because it had long been believed that the Sm^{3+} was responsible for the trapping states, and not as a center for recombination luminescence.

The three activator samples containing Eu^{2+}, Sm^{3+} and Sb^{3+} all exhibit the Eu^{2+} 589nm emission band and the Sb^{3+} 535nm emission band under 1.06μm optical stimulation. As the concentration of Sb^{3+} increases, the optically stimulated luminescence of both the Eu^{2+} ion and the Sb^{3+} ion decreases. At 1 mole percent Sb^{3+}, both emissions are very weak. The substitution of Sn^{2+} for Sb^{3+} in the triply activated series produces very faint optically stimulated luminescence.

D. Effect of Cation Host-Lattice Substituents on the Luminescence of the $MgS:Eu^{2+}:Sm^{3+}$ Phosphor.

Because of the chemical instability of the MgS host lattice in the presence of atmospheric moisture, the cations Zn^{2+} and Ca^{2+} were investigated as possible substituents for Mg^{2+} in the lattice. Both ZnS and CaS are more chemically stable than MgS and their Shannon-Pruitt cation radii are the closest to that of Mg^{2+} of all divalent cations*.

Additions of 10 mole percent Zn^{2+} to the $MgS:Eu^{2+}Sm^{2+}$ phosphor fired at 900°C diminished the ultraviolet excited

*Be^{2+} has a comparable radius to Mg^{2+}, but due to its toxicity, Be^{2+} was not investigated.

intensity of the 589nm Eu^{2+} peak and killed the 1.06μm optically stimulated luminescence. It was established by XRD that Zn^{2+} does not enter the MgS lattice in concentrations greater than 5 mole percent.

Additions of Ca^{2+} into the MgS lattice showed optically stimulated response to 1.06μm infrared stimulation, as well as bright ultraviolet excited luminescence.

A series of ten samples with the general formula $([Mg_{1-x},Ca_x]_{0.998},Eu_{0.001},Sm_{0.001})S$ were synthesized with x ranging from 0.1 to 1.0 in steps of 0.1. The samples were fired in argon bubbled through carbon disulfide at 900°C, the optimum temperature reported in the literature for CaS preparation.[11]

XRD of each of the samples revealed two phases: a CaS_{ss} phase and a MgS phase with little solid solution observed. Changes in the lattice parameters were used to calculate the range of solid solution assuming a Vegard's Law relationship. Approximate solubility limits are 3 mole percent of CaS into the MgS phase and 9 mole percent of MgS in the CaS phase. The variation of the solid solution limits with preparation temperature was not investigated.

All of the samples exhibited the Eu^{2+} band for CaS at 647nm, as reported by Nakao[9], while the $MgS:Eu^{2+}$ band at 589nm was observed only at Mg^{2+} concentrations not exceeding 60 mole percent or greater. This indicates the preference of the Eu^{2+} to substitute for Ca^{2+} rather than the Mg^{2+}

which is expected due to the larger ionic size of Ca^{2+}. There is no evidence of Sm^{3+} emission lines in any of the samples. The peak brightnesses of both the $MgS:Eu^{2+}$ and the $CaS:Eu^{2+}$ compositions are shown on Figure 15.

All ten samples show good OSL under 1.06 μm stimulation, with the OSL emission bands being identical to those observed under 250nm ultraviolet excitation. All optically stimulated emission peaks are shown in Appendix 3.

Each of the ten samples were immersed in 20 ml of water for 10 minutes, dried for 2 h at 200°C and the ultraviolet (250nm) excited luminescence reexamined. In all cases, only the 647nm $CaS:Eu^{2+}$ peak appeared. The CaS lattice is relatively chemically stable in the presence of H_2O, but small (3 mole percent) additions of Ca^{2+} do not appear to significantly enhance the chemical stability of MgS.

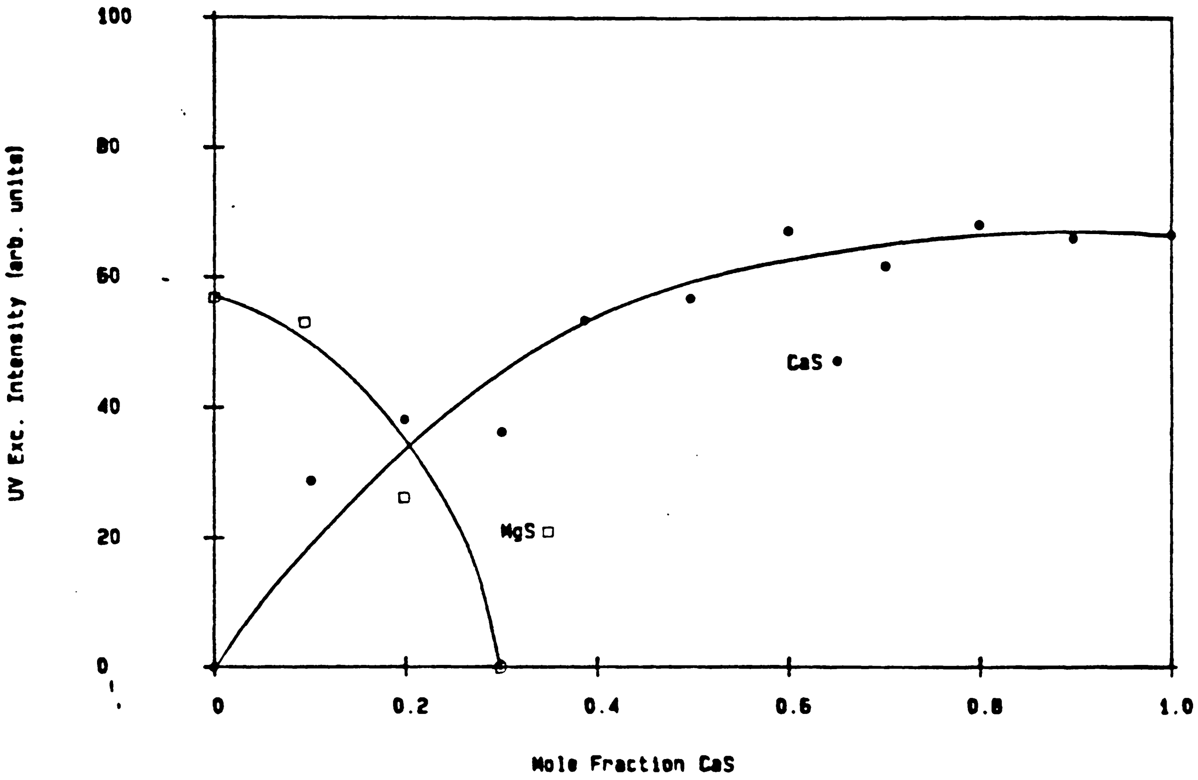


Figure 15. The effect of composition on the UV excited brightness of the $MgS:Eu^{2+}$ (589nm) peak and the $CaS:Eu^{2+}$ (647nm) peak for the $(Mg_{1-x},Ca_x)S:Eu^{2+},Sm^{3+}$ system.

V. DISCUSSION

It is evident from the UV excited spectra of MgS:Eu^{2+}:Sm^{3+} phosphors that the probability for electron-hole recombination at the Eu^{2+} center is much greater than that for the Sm^{3+}. Dexter[29] related transition probabilities to whether the transition is parity allowed (electric dipole) or parity disallowed (electric quadruple). Electric dipole transitions are orders of magnitude more probable than electric quadruple transitions, which explains the dominance of the Eu^{2+} emission in the UV (250nm) excited spectra.

Dexter[22] predicted that activator ions that undergo parity disallowed transitions are more likely to transfer energy by resonance to another center, which is responsible for the concentration quenching of the Sm^{3+} at low concentration and the increase in the UV stimulated brightness of the Eu^{2+} when small (0.01 mole percent) amounts of Sm^{3+} are present. The high thermoluminescent intensity at low concentrations of Sm^{3+} (0.01 mole percent) may also be attributed to the low concentration quenching of the Sm^{3+} since thermal stimulation of the MgS:Eu^{2+}:Sm^{3+} phosphor promotes recombination luminescence at the Sm^{3+} center. The thermoluminescence occurs when holes are either released from the V^- center (365 - 380K peak)[16] or from the Eu^{2+} center (662K peak)[12] and recombined with trapped electrons at the samarium ion. High concentrations of Sm^{3+} will quench this emission.

It is uncertain why Eu^{2+} concentrations above (0.01 mole percent) inhibit thermoluminescent response. One possible explanation is that with a large concentration of Eu^{2+} hole traps, a detrapped hole may be recaptured repeatedly by other Eu^{2+} holes until non-radiative recombination occurs at a native defect.

As expected there is no evidence of the (365-380K) peak in samples singly activated with Eu^{2+}, regardless of concentration. Since there is no need for charge compensation when Eu^{2+} replaces Mg^{2+}, cation vacancies and V^- centers do not form at appreciable concentrations.

The maximum optically stimulated (1.06 μm) intensity occurs at an Eu^{2+} and Sm^{3+} concentrations of 0.1 mole percent each. Optically stimulated recombination occurs at Eu^{2+} whose emission is not quenched at low concentrations (as is Sm^{3+}). It appears necessary that Sm^{3+} concentrations must exceed 0.01 mole percent in order to achieve optimum OSL intensity. Low Sm^{3+} concentrations do not provide ample amounts of trapping states for electrons to be released by optical stimulation.

The poisoning effect of Cl^- additions upon the UV excited and OSL brightness of the $MgS:Eu^{2+}:Sm^{3+}$ phosphor is difficult to explain, especially as it is a co-activator in structurally similar CaS, SrS and BaS phosphors. One possible explanation involves a discussion of native point defects existing in alkaline earth sulfides. According to Pauling's guidelines which predict the crystal structure of compounds of high ionic character from average ionic crystal radii, the ratio of the size of the S^{-2} (1.84 Å) to Mg^{2+} (0.72 Å) in octahedral coordination is too large for the NaCl structure to be predicted. The lattice may be highly strained with the S^{-2} ions very near each other because of the small size of the Mg^{2+} ions. A hard sphere model for the atoms would have the Mg^{2+} ions unable to adjoin all of the surrounding S^{-2} ions. The substitution of a trivalent activator ion will be much more likely to result in cation vacancies than anion interstitials in MgS. However, in CaS, SrS and BaS the size differential is not as great and anion interstitials may form. It is possible that interstital anion complexes such as $[Cl_S-S_i]$ or Cl_i may act as co-activators in CaS, SrS and BaS phosphors, while not present in MgS phosphors.

Aggregate defect centers may explain the change in the OSL stimulation spectra and the peak position of the high temperature glow curve upon the addition of Cl^- to the $MgS:Eu^{2+}:Sm^{3+}$ phosphor. The single defects Sm_{Mg} and Cl_S each have a +1 charge in the MgS lattices. In addition, both species would help relieve the inherent strain in the lattice, the Sm^{3+} increasing the cation size and the Cl^- decreasing the anion size. Defect clusters such as $[Sm_{Mg}-$

V_{Mg}-$Cl_S]^0$ would have a greater net positive charge than $[Sm_{Mg}$-$V_{Mg}]^{-1}$. An electron trapped in the former complex would need more energy to enter the conduction band than an electron trapped in the latter, necessitating higher energy, lower wavelength photons. The 840nm peak in the optical stimulation spectrum of $MgS:Eu^{2+}:Sm^{3+}:Cl^-$ may be due to electrons detrapping from the aforementioned aggregate centers.

Similarly, the defect cluster $[Eu_{Mg}Cl_S]^{+1}$ has a greater net positive charge than $Eu_{Mg}{}^0$. A hole trapped at the $[Eu_{Mg}Cl_g]^{+1}$ defect cluster would need less thermal energy to escape the trap due to Coulombic repulsion from the Cl_S^+ center.

The addition of Sb^{3+}/Sn^{2+} into the MgS:Eu:Sm phosphor produces characteristic emission peaks of both Eu^{2+} and Sb^{3+}/Sn^{2+}. The Sb^{3+} and Sn^{2+} have a more favorable emission peak wavelength (535nm) for photodetector response than the Eu^{2+} emission and it is desirable that electron-hole recombination occur at $Sb^{3+}(Sn^{2+})$ center. In the MgS:Eu:Sm:Sb phosphor, recombination occurs at both centers.

$$Eu^{3+} + e^- \longrightarrow Eu^{2+}$$

$$Sb^{4+} + e^- \longrightarrow Sb^{3+}$$

Differences in the peak intensity of the two activators are related to either the hole trapping probabilities of the Sb^{3+} and Eu^{2+} species or the electron-hole recombination probabilities of the Sb^{4+} and Eu^{3+} species.

The doubly activated phosphor MgS:Sm:Sb/Sn exhibited characteristic Sm^{3+} lines upon 1.06 μm optical stimulation indicating recombination at the Sm^{3+} center and optical detrapping of holes trapped at the hypothetical Sb^{4+} center.

The doubly activated phosphor MgS:Eu^{2+}:Sb/Sn exhibited characteristic bands of both Eu^{2+} and Sb^{2+}/Sn^{2+} after 1.06μm optical stimulation. This is unusual in that it is commonly accepted[16,17,19,20] that the electron traps are due to the Sm^{3+} with the optical stimulation peak at 1.07 μm. Whether the traps are due to intrinsic point defects, such as an V_S^{+2} [6] or whether both Sb or Eu may act both as charge carrier traps or recombination centers is unknown. Further work needs to be done in order to determine the exact mechanism for trapping and recombination.

It is found that the emission and excitation spectra of the isoelectronic species Sn^{2+} and Sb^{3+} are nearly identical. Lehmann[7] reported nearly identical emission and excitation spectra in CaS:Sb^{3+} and CaS:Sn^{2+} although Cl^- is needed as a co-activator in the CaS:Sn^{2+} phosphor. The two activators behave the same in UV excited and OSL emission studies in MgS.

Cation substitution for Mg^{2+} in the MgS host-lattice was unsuccessful in increasing the chemical stability of MgS. The primary reason is that neither of the two divalent cations examined, Ca^{2+} and Zn^{2+} were able to incorporate themselves into the MgS lattice in amounts greater than 9 percent. The most probable reason for the solid solution behavior of Ca in Mg is the larger ionic size of the Ca^{2+} (1.00 Å). It is thermodynamically more stable to form 2 phases. Zn^{2+} is close in size to Mg^{2+} but due to the greater electronegativity Zn-S bonds have a high covalent character, favoring the tetrahedral coordination of S^{-2} around Zn^{2+}.[30] Thus it is difficult to incorporate Zn^{2+} ions in the octahedral Mg^{2+} sites in MgS at Zn^{2+} concentrations greater than 5 atomic percent. In addition Zn^{2+}, isoelectronic with Cu^{1+}, poisons OSL in the MgS phosphor.

VI. CONCLUSIONS

The $MgS:Eu^{2+}:Sm^{3+}$ phosphor possesses properties which make it favorable for use in OSL personnel dosimetry, most notably the low $Z_{eff.}$, the proximity of the OSL stimulation peak (1.07 μm) to wavelength of the $YAG:Nd^{3+}$ laser, and excellent response to low levels of ionizing radiation.

The concentrations of Eu^{2+} and Sm^{3+} were optimized to attain maximum OSL response, but Cl^- additions which greatly enhance the UV excited intensity of the other alkaline earth sulfides, had a deleterious effect upon the UV excited intensity and the optically stimulated luminescence of the MgS:Eu:Sm phosphor system.

The addition of Sb^{3+} and Sn^{2+} create a second OSL emission band peaking at 535nm, which is favorable because the sensitivity of most photomultipliers is greatest in that range. However, the 589nm Eu^{2+} band could not be removed and it, continuously appears with the Sb^{3+}/Sn^{2+} band in the OSL spectra of triply activated samples.

Attempts to improve the chemical stability of the MgS phosphor by cation substitution were unsuccessful. The primary reason was the inability to incorporate substituents such as Ca^{2+} and Zn^{2+} into the MgS lattice in appreciable amounts.

Although the MgS:Eu:Sm phosphor shows promise for OSL personnel dosimetry application, further research is necessary to better understand the mechanisms of OSL in MgS-based phosphors and to improve their chemical stability.

Although the OSL properties are favorable, unless the chemical stability of the MgS:Eu:Sm phosphor can be improved, it is unlikely that the material will find widespread use as a practical OSL personnel dosimeter.

Summary

The MgS:Eu:Sm phosphor has properties that make it attractive as a candidate material for OSL personnel dosimeters such as low Z_{eff}, excellent response to low levels of ionizing radiation, and a favorable stimulation band at 1.06 μm.

The addition of Sb^{3+} adjusts the wavelength of the stimulated emission so as to correspond with the maximum sensitivity of most photodetectors with minimum loss of intensity. However, the instability of the host lattice and the subsequent production of toxic H_2S gas is a serious drawback. Unless the chemical stability of MgS may be improved, it is unlikely that the material will find use in practical personnel dosimetry.

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Appendix 1 - List of Starting Materials Producer

Producer	Product
Mallinckrodt Inc	99.9% $MgSO_4$ (anhydrous)
Fisher Scientific	99.9% $CaSO_4$ (anhydrous)
Rhone-Poulenc	99.99% Eu_2O_3
Rhone-Poulenc	99.99% Sm_2O_3
Johnson Matthey Inc.	99.9% $SmCl_3$ xH_2O
Fisher Scientific	99% $MgCl_2$
Johnson Matthey Inc.	99.9% Sb_2O_3
Fisher Scientific	99% $AgNO_3$
Fisher Scientific	99% Bi_2O_3
Johnson Matthey Inc.	99.9% SnO
Fisher Scientific	99% Cu_2O
Fisher Scientific	99% Pb_3O_4
Atomergic	99.9% ZnS
Fisher Scientific	reagent grade CS_2