Infrared-to-visible conversion following sub-band-gap excitation in MgS:Eu,Sm

K. Chakrabarti,* V. K. Mathur, and R. J. Abbundi
Naval Surface Warfare Center, White Oak, Silver Spring, Maryland 20903-5000
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We report here $Eu^{2+} \rightarrow Sm^{3+}$ electron transfer by tunneling in MgS:Eu,Sm. Subsequent to exposure to existing fluorescent or incandescent room light, optically stimulated luminescence which involves infrared-to-visible conversion is observed in this material. Room light excites the 480-nm absorption band of the Eu^{2+} ions which is associated with a transition from the $^8S_{11/2}(4f)$ ground state to the t_{2g} excited level. Some of the electrons subsequently tunnel from the t_{2g} level of the Eu^{2+} ions to the Sm^{3+} ions. We also report the optically stimulated luminescence from the V^- centers in this material.

I. INTRODUCTION

Over the last two decades, rare-earth-doped alkaline-earth sulfides have been studied both for basic and applied research interests. However, because of the recent development of TFEL (thin-film electroluminescence) technology and the advent of a number of infrared-laser sources, these materials have received renewed attention for potential uses as ACTFEL (alternating-current, thin-film electroluminescence) devices,[1,2] optically stimulated luminescent dosimeters,[3–6] infrared-laser detectors,[7] and random-access optically-erasable-memory devices.[8] Therefore, a thorough understanding of luminescence mechanisms and charge trapping in these materials is necessary. In our research endeavor to use these materials as laser-stimulated luminescent dosimeters and infrared sensors, we have carried out investigations on alkaline-earth sulfides doped with a number of rare-earth ions. It has been observed that the alkaline-earth sulfides doubly doped with Sm^{3+} and Eu^{2+} (or Ce^{3+}) ions possess thermally stable deep traps,[5,6,9] ideal for energy-storage purposes. Optically and thermally stimulated luminescence involving these deep traps has been reported[5,6] with a proposed model. We have also observed[10] that the V^- centers (cation vacancies with a hole trapped in each vacancy) are formed in the trivalent doped alkaline-earth sulfides when exposed to ionizing radiation, and the V^- centers are the origin of the shallow trap with associated thermoluminescence near 80 °C.

We have reported[5,6] optically stimulated luminescence (OSL) in MgS and CaS doubly doped with Eu (Ce) and Sm ions subsequent to exposure to ionizing radiation. Our present studies in MgS:Eu,Sm reveal that this material can be "charged" by room light; in other words, OSL can be observed subsequent to exposure to room light which does not cause band-to-band transitions. This makes this material attractive for commercial use as an infrared-laser sensor. We have also observed OSL from the V^- centers in this material. In this paper a physical explanation of the observed results is offered.

II. EXPERIMENTAL DETAILS

Magnesium sulfide was synthesized from anhydrous magnesium sulfate by CS_2 reduction. Details of the preparation and doping have been described elsewhere.[4,5] Experimental samples were prepared by depositing the phosphor on (25×25)-mm^2 glass substrates by sedimentation and coating the deposited thin layer by Dow-Corning 805 binder. The samples were mounted in a cryostat with a copper-Constantan thermocouple used to record the temperature. The data were taken at room temperature and at 77 K. The samples used for this study are MgS-I, which is MgS:Eu,Sm with an equal proportion of Eu^{2+} and Sm^{3+} ions (0.01 mol %), and MgS-II, which is doped with 0.01 mol % of Sm^{3+} ions only.

Optically stimulated luminescence measurements were taken using an EG&G PARC optical multichannel analyzer. To improve the signal-to-noise ratio, the silicon

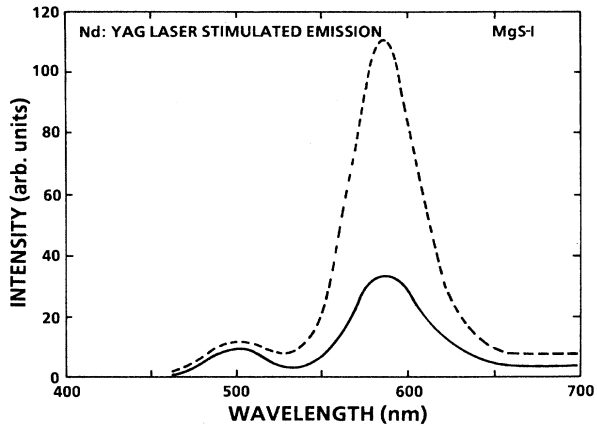

FIG. 1 OSL in MgS-I (MgS:Eu,Sm) at room temperature subsequent to exposure to 500-nm light for 300 s (solid line) and 3600 s (dashed line).

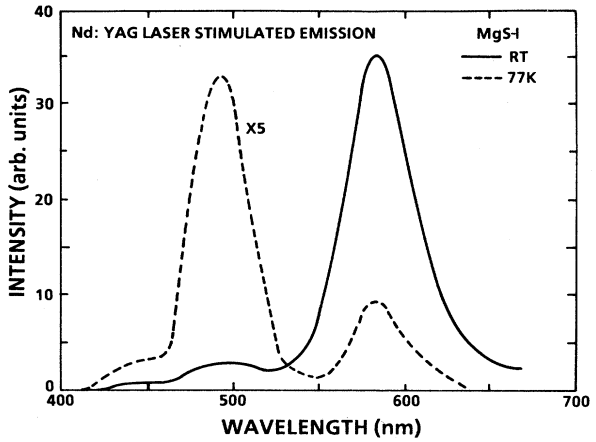

FIG. 2. OSL in MgS-I (MgS:Eu,Sm) at RT and at 77 K. In each case the sample was exposed to 500-nm light for 5 min prior to the OSL measurement.

diode array was cooled to −25 °C. Prior to an OSL measurement, the sample was exposed to selected wavelengths of light from a 300-w xenon source in conjunction with an Instruments SA, Inc. monochromator. A 1.06-μm neodymium-doped yttrium-aluminum-garnet (Nd:YAG) laser was used for optical stimulation.

III. EXPERIMENTAL RESULTS

We have made a series of OSL studies subsequent to exposing the sample to (350–650)-nm light selectively from the xenon lamp. It is observed that an exposure to 500-nm light generates the most intense OSL. Figure 1 shows the optically stimulated luminescence after MgS-I is exposed to 500-nm light for 5 min and 1 h, respectively.

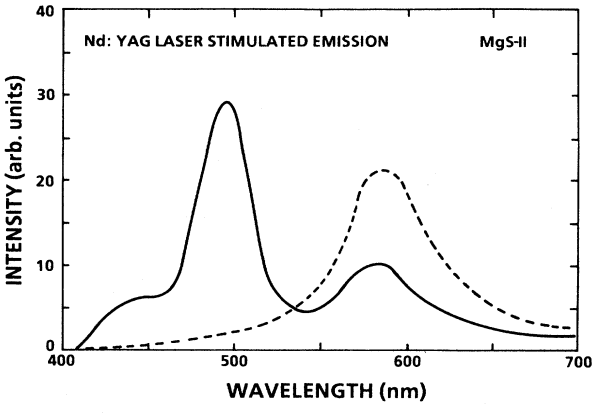

FIG. 3. OSL in MgS-II (MgS:Sm) at room temperature. The solid line shows the OSL observed after 5 min exposure to 500-nm light. The dashed line shows the OSL after the sample was heated to 100 °C for 5 min subsequent to exposure to 500-nm light for 5 min.

It is observed that the intensity of the OSL emission increases with exposure time and saturates at a time of 1 h exposure. The OSL has the dominant Eu^{2+} emission peaked at ~586 nm. There is, however, another emission which peaks at ~495 nm. Figure 2 shows the OSL at room temperature (RT) and at 77 K. In each case MgS-I was exposed to 500-nm light for 5 min prior to the OSL measurements. At 77 K the intensity of the 495-nm OSL peak increases by a factor of ~2.5, whereas the 586-nm peak is reduced by a factor of ~20. Figure 3 shows the OSL at RT subsequent to 5 min of exposure to 500-nm light in MgS-II. The dashed lines show the OSL taken after the sample is heated at 100 °C for 5 min subsequent to exposure to the 500-nm light.

IV. DISCUSSION

In MgS:Eu,Sm, OSL has been observed subsequent to exposure to uv radiation and the resulting emission is the characteristic Eu^{2+} emission. According to our proposed model[5] some of the electrons which are excited from the valence band to the conduction band by the uv light (MgS has a band gap of ~5.4 eV) are trapped by the Sm^{3+} ions which possess a net positive charge locally. When the uv-treated sample is stimulated with a Nd:YAG laser, the electrons are released from the Sm^{3+}-ion traps and are captured by the holes trapped at the Eu^{2+} ions, resulting in a characteristic Eu^{2+} broad emission.

In our present investigations, however, the OSL was generated by exposure to 500-nm light (Fig. 1) instead of uv light. The 500-nm light does not cause a band-to-band transition in MgS:Eu,Sm, but only excites the lower-energy absorption band of the Eu^{2+} ions. The Eu^{2+} absorption involves a $4f$-$5d$ transition and the $5d$ level splits into the e_g and t_{2g} levels as the Eu^{2+} resides in an O_h point-group symmetry in MgS. Therefore, Eu^{2+} absorption has two transitions, ${}^8S_{11/2}(4f)\rightarrow{}^2E_g(5d)$ and ${}^8S_{11/2}(4f)\rightarrow{}^2T_{2g}(5d)$, which are observed[7] as broad bands peaked at 260 and 480 nm, respectively. Structures due to the spin-orbit interactions are observed[7] in the excitation spectrum of the Eu^{2+} emission.

When this material is exposed to room light, the room light excites the 480-nm absorption band of the Eu^{2+} ions. OSL is observed subsequent to this exposure on stimulating with a Nd:YAG laser. We have observed that 500-nm light generates the strongest OSL in MgS:Eu, Sm, as shown in Fig. 1. Since the t_{2g} level lies below the e_g level in O_h symmetry, ionization from the t_{2g} level to the conduction band is highly unlikely. These results strongly suggest that the electron transfer from Eu^{2+} to Sm^{3+} takes place by tunneling. Some of the excited electrons from the t_{2g} level of the Eu^{2+} ions tunnel to the Sm^{3+} ions, where they remain trapped until stimulated by the ir light. The stimulation spectrum of the electrons from the Sm^{3+}-ion traps shows a broad band in the region 750–1350 nm. The electron transfer from Eu^{2+} to Sm^{3+} ions can also be seen by bleaching the sample with 500-nm light. It is observed[7] that bleaching by the 500-nm light reduces the intensity of Eu^{2+} and Sm^{3+} emissions. This suggests that the electrons tunnel from

the t_{2g} level of the Eu^{2+} ions to the Sm^{3+} ions, quenching the emission of both the Eu^{2+} and the Sm^{3+} ions. We also have observed[7] that increasing the concentration of the Sm^{3+} ions in MgS:Eu,Sm decreases the intensity of the Eu^{2+} emission when excited by 480-nm light. This also indicates that more electrons are transferred from the t_{2g} level of Eu^{2+} to Sm^{3+}, when more Sm^{3+} ions are present in the sample.

Besides the 585-nm Eu^{2+} emission, the OSL spectrum also shows an emission peaked at 495 nm which increases at 77 K (Fig. 2). Since the optically stimulated luminescence results when the stimulated electrons from the Sm^{3+}-ion traps recombine with the trapped holes, the origin of the 495-nm OSL should also be a trapped hole center. We have observed in TL measurements that besides the hole release from the Eu^{2+} ions, which is associated with a TL peak[5] at $\sim 200\,^{\circ}C$, there is a TL peak at $\sim 80\,^{\circ}C$ due to the thermal destruction of the V^- centers.[10] With this in mind and observing that the 495-nm OSL increases at 77 K, where the V^- centers are more stable than at room temperature, we performed two sets of experiments. We used the sample MgS-II where only the Sm^{3+} ions are doped deliberately so that more V^- centers are created in the sample. In MgS-I the holes are trapped predominantly by the Eu^{2+} ions and the cation vacancies. In MgS-II the absence of Eu^{2+} ions minimizes the competition for hole trapping by the cation vacancies and as such more V^- centers are produced in this sample. In the first set of experiments, we exposed the sample to 500-nm light and performed the OSL measurement by stimulating with a Nd:YAG laser. The OSL intensity of the 495-nm peak increased considerably (Fig. 3), thus increasing the possibility that the V^- center is the origin of this OSL. A feeble but unmistakable Eu^{2+} emission was also observed in the OSL, suggesting that some Eu^{2+} ions were present in the material as an impurity. Chemical analysis shows[11] that Eu^{2+} is the chief impurity present in Sm_2O_3, the starting material used for doping the Sm^{3+} ions.

In the second set of experiments, we exposed MgS-II to 500-nm light for 5 min and then heated to 100 °C for 5 min prior to the OSL measurements. No 495-nm OSL was observed this time. It is known that the thermal destruction of the V^- centers occurs near 80 °C.[10] Therefore, upon heating the sample to 100 °C the V^- centers are destroyed and as such no OSL emission from them is observed. This result confirmed the fact that the 495-nm OSL emission is due to the radiative recombination of electrons and holes at the V^- centers. An increase of Eu^{2+} OSL emission after heating to 100 °C can be attributed to the fact that some of the holes released thermally from the V^- centers can be retrapped by the Eu^{2+} ions, thus increasing the Eu^{2+} OSL emission. This result also supports our earlier assignment that the Eu^{2+} OSL emission results from the deeper trap, which is thermally stable up to $\sim 200\,^{\circ}C$.

Our results show unambiguous evidence of $Eu^{2+} \rightarrow Sm^{3+}$ electron transfer, which does not involve the conduction band, and the OSL from the V^- centers. However, it is not clear how the 500-nm light created V^- centers and did so more effectively than the uv light. It is possible that 500-nm light excites the S^{2-} ions adjacent to the cation vacancies and the electrons escape to Sm^{3+} ions and the holes are trapped at the cation vacancies, forming V^- centers. It is also noteworthy that no significant Eu^{2+} OSL emission is observed at 77 K in the Eu^{2+}-rich MgS-I, suggesting that the $Eu^{2+} \rightarrow Sm^{3+}$ electron-transfer tunneling process is thermally assisted and is favored at room temperature. Besides the OSL due to the Eu^{2+} ions and the V^- centers, a weak OSL peaked at ~ 440 nm is also observed (Figs. 2 and 3). The exact origin of this OSL is not known; however, it may be due to the formation of a V^--center impurity complex or V^0 center (cation vacancy with two holes trapped) in this material.

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*On leave from Southwestern Oklahoma State University, Weatherford, OK 73046.

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