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Brief Reports

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Evidence of V^- centers in trivalent rare-earth doped MgS

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A thermoluminescence (TL) peak near 80 °C is observed in MgS singly doped with a different trivalent rare-earth ion (Sm^{3+}, Ce^{3+}, Tb^{3+}) and exposed to ionizing radiation at room temperature. It appears that the V^- center, as in alkaline-earth oxides, is the origin of the TL peak. A suggested mechanism of charge trapping to explain the observed results is that the electrons are trapped at the trivalent ions and the holes at the vacancies. On heating the sample over 100 °C, thermal destructions of the V^- centers occur, and the released holes recombine with the trapped electrons at the Sm^{3+} (Ce^{3+}, Tb^{3+}) ions, leading to the luminescence that is characteristic of Sm^{3+} (Ce^{3+}, Tb^{3+}) ions.

I. INTRODUCTION

Radiation-induced defect centers such as *F*-type centers (anion vacancies with trapped electrons) and *V*-type centers (cation vacancies with trapped holes), as well as self-trapped hole centers or V_k centers and interstitial associated hole centers known as *H* centers, have been thoroughly investigated in alkali halides,[1] alkaline-earth fluorides,[2] and in simple oxides[3] such as MgO, CaO, and Al_2O_3. As a result of these studies, the mechanisms[1-3] of the defect production are well understood. It is known that the ionizing radiation can create both electron centers as *F* centers and hole centers as V_k and *H* centers in alkali halides and alkaline-earth fluorides. There is no evidence of *F* center productions in oxides by ionizing radiation. However, in alkaline-earth oxides with trivalent ion impurities, ionizing radiation produces V^- centers[3-6] (a cation vacancy with a trapped hole shared by an adjacent oxygen ion) and causes a change in charge state of the impurity ion. The cation vacancies in alkaline-earth oxides as in MgO are formed when the trivalent ions as Fe^{3+} replace the divalent Mg^{2+} ions in the lattice. On exposure to ionizing radiation, the charge state of a trivalent ion changes as it becomes a divalent ion and the hole is trapped at the Mg^{2+} ion vacancy with the hole being shared by the next neighbor oxygen ion.

Although considerable progress has been made to characterize the point defects in these materials,[1-3] relatively little has been done in alkaline-earth sulfides. Alkaline-earth sulfides, doped with rare-earth ions, have been used[7-9] for more than a decade as efficient phosphors for cathodoluminescence and electroluminescence devices. Because of the availability of different types of laser sources, these materials have recently[10-13] received added attention for use as optically stimulated radiation dosimeters. Consequently, a need to develop a better understanding of the properties and production of radiation defects in alkaline-earth sulfides has increased more than ever. In our previous study of MgS doubly doped with Ce^{3+} (Eu^{2+}) and Sm^{3+}, we have reported[12,13] unambiguous evidence of hole trapping in Ce^{3+} (Eu^{2+}) ions and electron trapping in Sm^{3+} ions, after the sample is exposed to ionizing radiation at room temperature. The thermal destruction of the trapped holes at Ce^{3+} (Eu^{2+}) ions is the cause of the higher temperature thermoluminescence (TL) peak ~200 °C in these materials. It is the high-temperature TL peak that makes these materials ideal for radiation dosimetry and storage phosphors. However, in both MgS:Ce,Sm and MgS:Eu,Sm, we also observed a TL peak ~80 °C. As a part of our continued research in this material, we have further investigated the origin of this lower temperature TL peak. We have studied a series of MgS samples singly doped with the rare-earth ions Ce^{3+}, Sm^{3+}, Tb^{3+}, and Eu^{2+}. All the trivalent doped MgS, exposed to ionizing radiation at room temperature, exhibit a TL peak near 80 °C. This peak, however, is not observed in MgS doped with divalent Eu^{2+}. In all trivalent ion doped MgS, exposed to ionizing radiation at room temperature, a broad optical-absorption band in the region 550 to 690 nm developed which disappeared on heating the sample over the TL peak. Also, the TL emission was found to be characteristic of the trivalent ion present in the sample. All these results are similar to the work reported[3-6] in MgO strongly suggesting the creation of the hole trapped V^- center in irradiated trivalent rare-earth doped MgS.

II. EXPERIMENTAL DETAILS

Magnesium sulfide was synthesized from anhydrous magnesium sulfate by CS_2 reduction in the presence of argon. Details of the preparation and doping have been described elsewhere.[10,13] Experimental samples were prepared by depositing the phosphor on 25×25 mm^2 glass substrates by sedimentation and coating the deposited thin layer ~100 μm by Dow Corning 805 binder. Thermoluminescence measurements were made by a Harshaw reader Model 2000 B and C, after the samples were irradiated by ionizing radiation at room temperature, using a Hg vapor lamp. The heating rate in each case was 5 °C/sec and the TL glow curves were recorded by an X-Y recorder. The study of the spectral dependence of the emissions from the TL peak was performed by heating the sample near the TL peak on a hot plate. The sample mounted on a brass disk was placed on the hot plate and a thermocouple was attached to the disk to record the temperature. The TL emissions were detected by an EG&G PARC optical multichannel analyzer. To improve the signal-to-noise ratio, the silicon diode array was cooled to -25 °C.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Figure 1 shows the TL glow curves of MgS:Ce^{3+}, MgS:Sm^{3+}, and MgS:Tb^{3+}. The TL peaks of these samples are observed at ~65, ~70, and ~75 °C, respectively. The spectral dependence of the TL emission is shown in Fig. 2. For MgS:Sm^{3+}, the TL emissions are at 564, 604 and 656 nm and can be identified as Sm^{3+} $4f$-$4f$ transitions from $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ ground states.[12,13] For MgS:Tb^{3+}, the TL emissions are at 490, 545, 578, 630, and 668 nm. These $4f$-$4f$, $^5D_4$ to ^7F_J manifold transitions of Tb^{3+} ions are well known.[14,15] For identified TL emissions in our case, transition to ^7F_J ground states have J values from 2 to 6. In the case of MgS:Ce^{3+}, the $5d$ orbit in O_h crystal field symmetry splits into e_g and t_{2g} levels and the Ce^{3+} emission has a doublet $^2T_{2g}(5d) \rightarrow {}^2F_{7/2}, {}^2F_{5/2}(4f)$ emission[8,13,16] with a separation of ~0.23 eV. The TL emissions can be recognized as a broad Ce^{3+} emission at ~520 nm due to the transition to the $^2F_{5/2}$ ground state and the second emission band due to the transition to the $^2F_{7/2}$ ground state occurs at ~580 nm. There are three other weak emission bands observed exactly at the positions of Sm^{3+} emissions discussed earlier, suggesting the presence of Sm^{3+} ions as an impurity in our Ce^{3+}-doped sample. Also, in all three samples, TL emissions have a band with a peak at ~430 nm, which is particularly evident in MgS:Tb^{3+}. The origin of this emission, which is very likely due to a common impurity present in all the samples, is not known.

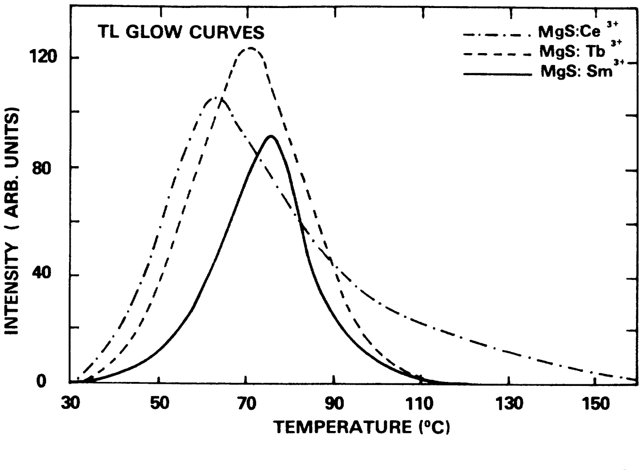

FIG. 1. Thermoluminescence glow curves of MgS:Ce^{3+}, MgS:Tb^{3+}, and MgS:Sm^{3+}.

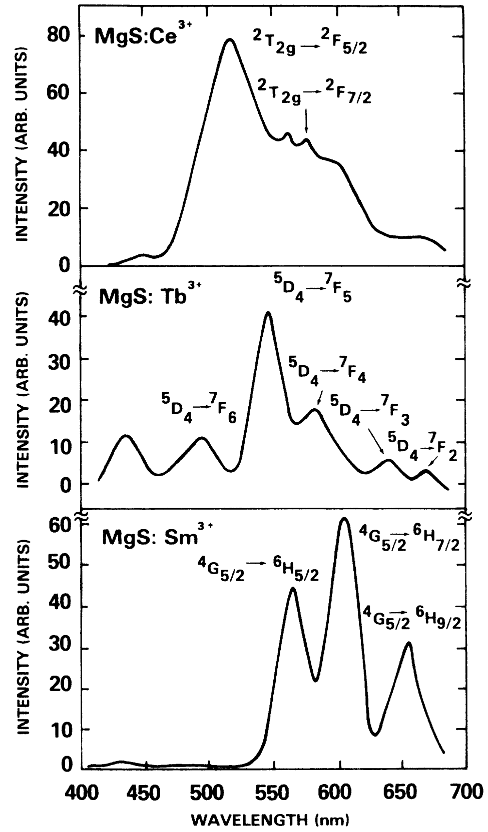

FIG. 2. Thermoluminescence emission spectra of MgS:Ce^{3+}, MgS:Tb^{3+}, and MgS:Sm^{3+}.

The above results indicate that the V^- centers are generated in these trivalent rare-earth doped phosphors after the samples are exposed to ionizing radiation at room temperature. When a trivalent rare-earth ion replaces a divalent Mg^{2+} ion, a charge compensation is necessary in the lattice. This charge compensation is attained by a cation vacancy produced when two Mg^{2+} ions are replaced by two trivalent ions. The charge compensation in the form of sulfur interstitial is unlikely because of the relatively large size of the sulfur ions.

Exposure to ionizing radiation in MgS of band gap ~5.4 eV causes a band-to-band transition, i.e., an electron is excited from the valence band to the conduction band. This electron is subsequently trapped by a trivalent rare-earth ion Sm^{3+} (or Ce^{3+} or Tb^{3+}) as this ion possesses a local positive charge relative to the divalent lattice and acts as an electron trap. The hole that is left behind is then trapped by a cation vacancy, the hole being shared by the next neighbor sulfur ion forming a V^- center. The thermal destruction of these V^- centers occurs ~80 °C and the released holes from the V^- centers recombine with the trapped electrons at the trivalent ions resulting in a thermoluminescence glow curve. This model is supported by the TL emission which is characteristic of the trivalent ion present in the material. A similar TL peak ~100 °C is also observed from the thermal destruction of V^- centers in MgO. Also, in the case of MgO, the cation vacancies are produced when the trivalent impurity ions replace the divalent Mg^{2+} ions and on γ or ultraviolet (uv) irradiation V^- centers are produced. The V^- center is also reported in other alkaline-earth oxides[17,18] and in Al_2O_3 (Ref. 19) and in $Y_3Al_5O_{16}$.[20,21]

The described mechanism of charge trapping can be represented by the following: (1) After the sample is irradiated by ionizing radiation

$$Sm^{3+}\ (Ce^{3+},Tb^{3+})+e^- \rightarrow Sm^{2+}\ (Ce^{2+},Tb^{2+})\ ,$$

$$\text{Cation vacancy}+S^{2-}+e^+ \rightarrow V^-\text{center}\ ;$$

(2) On heating the sample over 100 °C

$$V^-\ \text{center} \rightarrow \text{cation vacancy}+S^{2-}+e^+\ ,$$

$$Sm^{2+}\ (Ce^{2+},Tb^{2+})+e^+ \rightarrow Sm^{*3+}\ (Ce^{*3+},Tb^{*3+})\ ,$$

$$Sm^{*3+}\ (Ce^{*3+},Tb^{*3+}) \rightarrow Sm^{3+}\ (Ce^{3+},Tb^{3+})+h\nu\ .$$

It is also known[3] that the V^- center in MgO is associated with a broad optical-absorption band with a peak ~2.3 eV which is destroyed on heating the material over 100 °C. We also observed a broad optical-absorption band ranging from 550–690 nm in all our trivalent rare-earth doped MgS samples. The intensity of this band, however, is weak and is only observed in the difference curve of after and before uv irradiation of the sample even though the oscillator strength of V^- centers is high and is reported[22] to be 0.07–0.1 in alkaline-earth oxides. The low intensity of the optical density signal can be attributed to the small number of V^- centers created in our samples due to their small thickness ~100 μm. It should also be noted that only a small fraction of the cation vacancies change to V^- centers after uv irradiation. This band disappears on annealing the samples over 100 °C suggesting that it is due to V^- centers.

IV. CONCLUSION

We have presented in this paper the first evidence of the V^- centers in an alkaline-earth sulfide. Optical characteristics of this suggested V^- center in MgS are very similar to that of well-established V^- centers in MgO. However, since a V^- center is paramagnetic, electron-spin resonance study in this material is necessary to acquire more information about this suggested V^- center.

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