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LUMINESCENCE FROM SELF-TRAPPED HOLES IN MANGANESE-DOPED CALCIUM FLUORIDE SINGLE CRYSTALS

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Thermally stimulated luminescence (TSL) and electron spin resonance (ESR) measurements on X-irradiated CaF_2:Mn (0.1 wt.%) single crystals have been conducted in the interval 70 to 300 K. Prominent TSL peaks occur near 150 K (345- and 495-nm emission) and 200 K (predominantly 495-nm emission) with thermal decay of ESR centers at these same temperatures. Taken collectively the data suggest that 150 K TSL emission is due to mobile holes from V_K centers recombining with both trapped electrons and Mn^+ ions, *i.e.*, $V_K + e^- \rightarrow$ 345-nm emission, and $V_K + Mn^+ \rightarrow (Mn^{2+})^* + h\nu$ (495-nm emission). Additionally, H centers are formed by transformation of V_K centers. At 200 K, holes from H centers recombine with Mn^+ to produce excited-state $(Mn^{2+})^*$ which decays by emitting 495-nm radiation.

1. INTRODUCTION

Previous TSL work[1] on CaF_2:Mn has shown that in the interval 77 to 300 K the most intense glow occurs near 200 K. Predominant emission is characterized by a nearly Gaussian-shaped peak with maximum at 495 nm, and is attributed[2] to the deexcitation of an excited Mn^{2+} ion [$(Mn^{2+})^* \rightarrow Mn^{2+} + h\nu$ (495 nm)]. Optical absorption studies[3] in the same temperature interval have identified a band at 450 nm which thermally decays at 200 K and is associated with Mn^+ ions. ESR experiments[4] on irradiated CaF_2:Mn also showed that Mn^+ resonance signals thermally decayed at 200 K. These results suggested that 200 K TSL was due to mobile holes from H centers recombining with Mn^{2+} ions yielding 495 nm emission. In addition to the Mn^+ ESR signal, a second resonance which thermally decayed near 150 K was observed but not identified. In the present work we present TSL and ESR data which show that thermal decay of this ESR signal is correlated with the 150 K TSL glow peak and that recombination luminescence involves self trapped holes (V_K centers).

2. EXPERIMENTAL

Single crystals of CaF_2 containing 0.1 ± 0.01 wt.% Mn, obtained from Optovac, Inc., were used in this investigation. Irradiation was provided by an x-ray machine operating at 40 kVp and 25 mA with an exposure rate at the sample site of 1.4×10^3 R min^{-1} (0.36 C $kg^{-1}min^{-1}$). ESR data were taken on both X-band ($\nu \simeq 9$ GHz) and K-band ($\nu \simeq 25$ GHz) spectrometers. Isochronal thermal annealing of the ESR signals was performed by warming the sample to a selected temperature and maintaining that value for a given time period. Subsequently the sample was cooled to 70 K and the resulting spectra recorded. Bandpass filters were used in conjunction with a high pressure mercury-vapor lamp (500 W) to provide selective photobleaching of the resonance signals.

3. RESULTS AND DISCUSSION

Typical low-field ESR spectra of CaF_2:Mn X irradiated at 70 K are shown in Fig. 1. Data were taken at 70 K with a K-band spectrometer operating at $\nu = 25.136$ GHz. Thermal decay of the Mn^+ signal has been previously discussed[4] and we concentrate on the resonance lines labeled II, III, and IV. As shown in the lower portion of the graph, these lines are highly dependent on the angle between the applied magnetic field and the (110) crystal axis. From the measured field position of these resonance lines with respect to the rotation angle, and from their intensity ratios, it is concluded that these hyperfine spectra are typical of a

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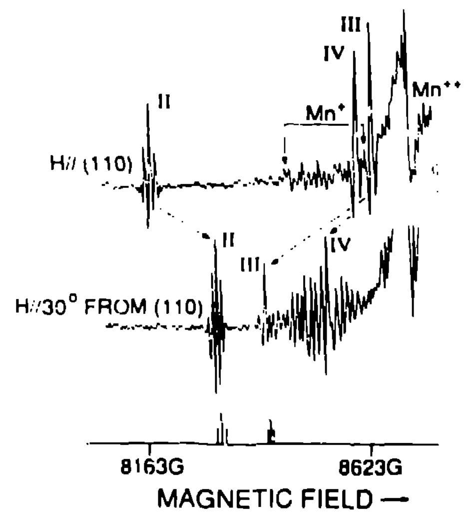

FIGURE 1
Low field ESR spectra of irradiated CaF_2:Mn.

hole trapped by two nearest- and next-nearest-neighbor fluorine ions, all lying along the same F_2^- molecular axis. The three signals II, III, and IV correspond to the three different orientations of a self-trapped hole with respect to magnetic field. Furthermore, these lines are all photobleached when exposed to 315-nm radiation, and are thermally destroyed at 150 K. Based on these results we propose a model to explain the observed 150 and 200 K TSL emission of CaF_2:Mn.

Irradiation at 70 K produces V_K and H centers, Mn^+ and Mn^{3+} ions, and electrons. A V_K center consists of a self-trapped hole localized between near neighbor substitutional F^- ions, i.e., it can be viewed as a F_2^- molecular ion oriented along the crystallographic ⟨100⟩ direction. The H center, similar to the V_K center, is a self-t[illegible]ed hole located between an interstitial F^- and nearest neighbor substitutional F^- ion, oriented along a ⟨111⟩ direction. Self trapped excitons (electrons trapped in the positive potential of V_K centers) may also be produced by the radiation. Upon warming CaF_2:Mn to 150 K, three processes occur: (1) holes from the V_K centers become mobile and recombine with trapped electrons whereby they produce TSL emission at 345 nm [$V_K + e \rightarrow h\nu$ (345 nm)], (2) V_K center holes recombine with Mn^+ ions yielding excited state Mn^{2+} which decays with characteristic 495 nm emission [$V_K + Mn^+ \rightarrow (Mn^{2+})^* + h\nu$ (495 nm)]; and (3) some fraction of the V_K centers reorient to produce the more thermally stable H centers [V_K (reorient.) $\rightarrow H$]. Upon further warming to near 200 K, the H-center holes become thermally unstable and migrate to Mn^+ ions; they recombine, producing excited-state Mn^{2+} ions and concomitant 495-nm emission [$H + Mn^+ \rightarrow (Mn^{2+})^* + h\nu$ (495 nm)].

This model explains the TSL and ESR observations and is similar to one previously suggested by Beaumont *et al.*[5] to describe TSL in thulium-doped CaF_2. We note that they identified a broad, asymmetric emission band peaking near 280 nm which was ascribed to self-trapped exciton (STE) luminescence. This luminescence results from recombination of a self-trapped hole with the electron trapped in its positive potential, and should be somewhat different than ordinary electron-hole recombination. Unfortunately our data do not allow us to make such a distinction. Nevertheless, we suggest that 345-nm emission in CaF_2:Mn is associated with V_K centers rather than cerium impurity[6] as has been recently proposed.

4. CONCLUSIONS

A model describing the 150 and 200 K TSL emission in X-irradiated CaF_2:Mn has been presented. At 150 K, TSL emission spectra peaks occur at 345 and 495 nm, and are attributed to V_K-center holes recombining with electrons and Mn^+ ions, respectively. Some of the V_K centers are also transformed to H centers. Near 200 K the H-center holes become thermally unstable and recombine with Mn^+ ions, yielding 495-nm emission. No distinction is made between STE luminescence and ordinary hole (V_K center)-electron recombination. The 345-nm emission in CaF_2:Mn is not associated with cerium.

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