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A new thin-film electroluminescent material—ZnF$_2$:Mn[a]

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Both ac and dc orange (580 nm) electroluminescence (EL) are reported for thin films of ZnF$_2$:Mn sandwiched between SiO semi-insulating films. All layers are formed by vacuum evaporation and no postdeposition annealing is required. Unique power input and efficiency-vs frequency characteristics are observed, in part due to the 0.1-s lifetime of excited Mn in ZnF$_2$; hysteresis in the brightness-voltage characteristic occurs. The brightness and power efficiency are found to be, respectively, 10 f L and 0.5% under suitable operating conditions.

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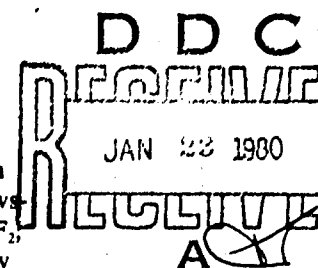
High-field collision-excitation electroluminescence (EL) has become a current area of active research as a result of the application of thin-film technology to form relatively stable EL devices with power efficiencies approaching 1% and with hysteresis in the brightness-voltage characteristic permitting information storage as well as display.[1] The major research has involved evaporated ZnS:Mn sandwiched between sputtered or electron-beam evaporated Y$_2$O$_3$[1-3]; similar devices have been made with ZnSe : Mn[4]; related work has been reported on crystals of CdF$_2$: Mn in MIS structures[5]; EL has been studied with rare earth dopants in place of Mn in these materials[6]—in all the aforementioned, a high temperature postgrowth anneal is required.

ZnF$_2$: Mn is unique among luminescent materials in being capable of rather efficient cathodoluminescence in the form of transparent thin films formed by vacuum evaporation.[7] No postdeposition anneal is needed. Its lower refractive index minimizes the internal trapping of the emission which reduces substantially the efficiency of ZnS thin films. The ZnF$_2$ and ZnF$_2$: Mn have the rutile structure and are weakly N-type semiconductors with low electron mobility;[8]

thus, these materials differ markedly in structure and electronic properties from CdF$_2$ and CdF$_2$: Mn.

The layered thin films were deposited in sequence on conducting Corning glass 7059 (SnO$_2$ coated to 100 Ω/square resistance) maintaining the vacuum at less than 2×10^{-5} Torr. Both the ZnF$_2$: Mn and SiO were outgassed before evaporation. The ZnF$_2$: Mn used in the evaporation had been mixed by weight from ZnF$_2$ and MnF$_2$, sintered at 800 °C and ground to a powder. Compositions investigated were 0.5–5-mol% MnF$_2$. The substrate was slightly above room temperature. Typical sequential deposits were 5000 Å of SiO, 2000 Å of ZnF$_2$: Mn, and 5000 Å of SiO. Selected edges were masked in order to make electrical contacts. Finally, the second electrode of aluminum was deposited by evaporation through a mask.

The SiO is only semi-insulating, so that dc EL, as well as ac EL, is observed. The highest efficiencies are measured at low frequencies, e.g., 10 cps. The current I in the external
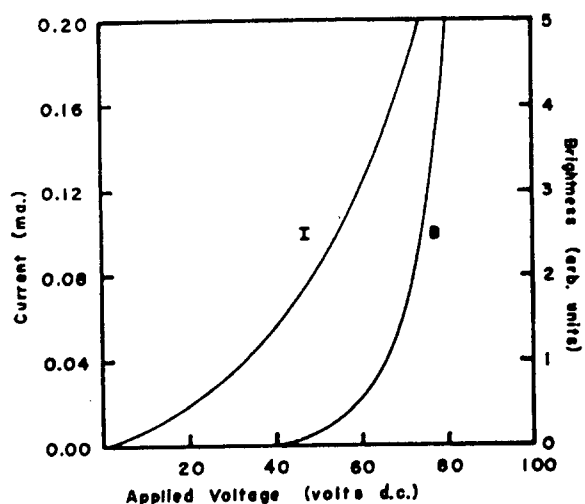

FIG. 1. Current I and brightness B versus applied dc voltage V for ZnF$_2$:0.011 Mn with the typical SiO and fluoride thicknesses.
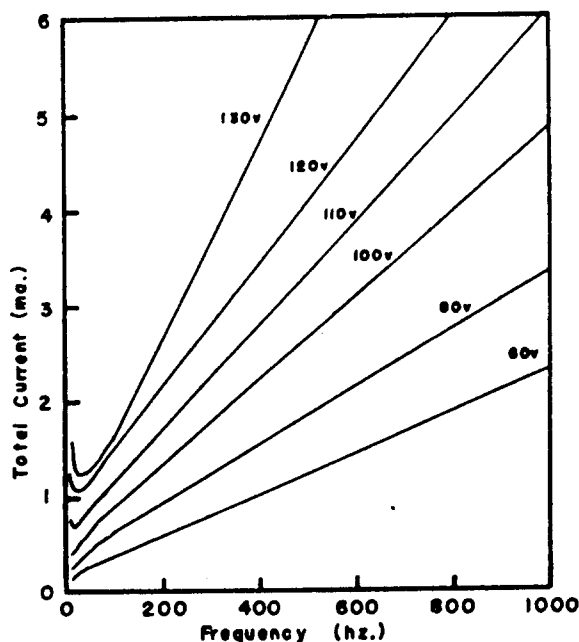

FIG. 2. Total current I versus frequency f for different applied ac voltages V_{rms}. 90% of the data points fall within $\pm$ 20 cps and $\pm$ 0.1 ma for the curve at highest V and within $\pm$ 10 cps and $\pm$ 0.02 ma for the curve with lowest V.
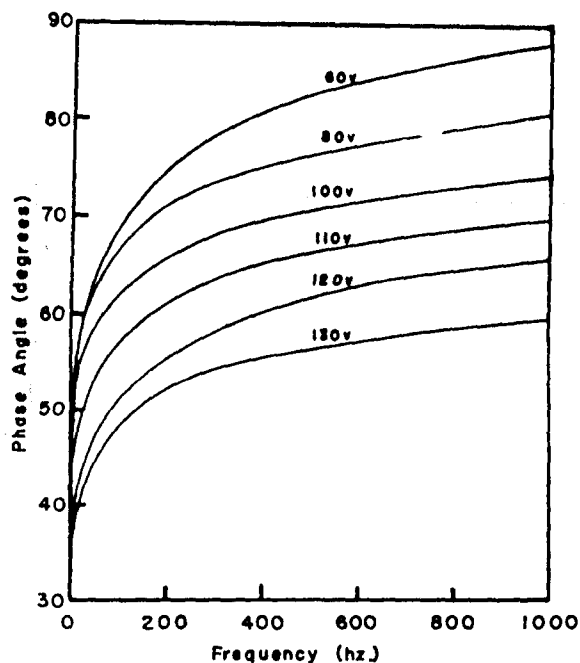
FIG. 3. Phase angle ϕ versus frequency f for different V_{rm}. 90% of the data points fall within $\pm$ 20 cps and $\pm$ 3° of the fitted curves.

FIG. 4. Brightness-voltage hysteresis curve at 500 cps for ZnF_2 : 0.016 Mn.

circuit is shown in Fig. 1 for dc, and as a function of frequency for applied ac voltages V in Fig. 2. The brightness, B versus V is also shown on Fig. 1. In order to obtain the input power P for ac the phase difference ϕ between I and V was measured on a dual trace Tektronix 545 scope and is plotted versus f in Fig. 3 for different V. The device responds electrically like a non-Ohmic resistor in parallel with a capacitor so that with increasing f the current generally becomes more capacitive, but at higher V the current remains more resistive to higher f. The non-Ohmic character is evident from the dc measurements. Thus, from the data in Figs. 2 and 3, the P can be obtained: $P = IV \cos\phi$. Except for some structure at low f, P is approximately linear with f, with greater slope at higher V.

The brightness B was measured as a function of V and f. Hysteresis in B (V) was observed and is shown in Fig. 4. This characteristic is similar to those reported for ZnS : Mn[1,2] and for ZnSe : Mn.[4] The electrical characteristics described in the preceding paragraph are for the decreasing voltage B (V) curve. The emission spectrum of the ZnF_2 : Mn with EL excitation is the same as previously reported for photo- and cathode-ray excitation, peaking at 580 nm.[7]

Absolute brightnesses were measured by two independent methods: comparison with a standard lamp illuminating a diffusing screen, and a calibrated Tektronix J16 digital photometer. Brightnesses of 10 fL were attained with reasonable stability; higher values resulted in deterioration of present devices. Combined with power input data, power efficiencies η of 0.5% were obtained at low frequencies, e.g., 10 –30 cps. At higher f, η decreases approximately as $1/f$.
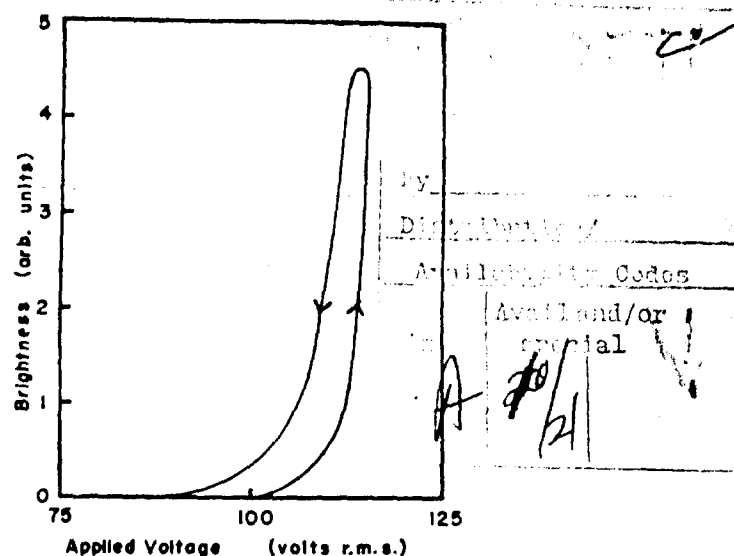
The $\eta \propto 1/f$ and $P \propto f$ at the higher f mean, of course, constant B at constant V, independent of f, suggesting saturation. From the radiative lifetime of 0.1 sec for Mn in ZnF_2 : Mn' and for concentrations of 1-mol% Mn, saturation of a 2000-Å-thick layer is predicted at 10 mW of radiation/cm^2. We observe as much as 0.1 mW/cm^2 of radiation which means that 1% of the Mn are homogeneously excited simultaneously or that 1% of the volume is excited to saturation. This estimate neglects internal trapping and absorption in the SiO. No inhomogeneities were observed microscopically under normal conditions of excitation.

Summarizing, layered thin-film ZnF_2 : Mn device electroluminescence at low frequencies with efficiencies approximately equal to those of other high field EL devices and with hysteresis in the B (V) characteristic have been observed. We are investigating ZnF_2 : Mn devices with better insulating layers to attain higher efficiency and stability. The absence of a postdeposition anneal allows for the possibility of deposition on low melting substrates such as plastics.

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