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LOW-VOLTAGE CATHODOLUMINESCENT PROPERTIES OF EUROPIUM-ACTIVATED ANION-DEFICIENT FLUORITES

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ABSTRACT

We have examined the optical bandgap, particle size distribution, photoluminescence spectra, and cathodoluminescent response of fifteen phosphors that contain transition-metal and main-group sensitizers. We determined luminance versus applied voltage curves for electron energies from 5 to 1000 eV. Seven phosphors exhibit threshold voltages less than 110 V. $\text{Y}_{1.96}\text{Eu}_{0.04}\text{O}_3$ exhibits a threshold voltage of 13 V and, at 300 V, displays a luminance of 25 fL and a luminous efficiency of 0.02 lm/W.

INTRODUCTION

The flat-panel display market generated \$4.7 billion in 1993 and is conservatively projected to grow 10.1% annually to \$7.6 billion by 1998.¹ Four display types account for nearly all the revenue: liquid crystal (LCD), electroluminescent (ELD), vacuum fluorescent (VFD), and plasma display panels (PDP).²

A key objective of flat-panel technology is to replace the bulky but ubiquitous cathode ray tube (CRT) display. Flat-panel displays based on low applied voltage field-emitter arrays (FEAs) hold great promise for thin, full-color, high definition devices³ that offer all the advantages of the conventional CRT in a more attractive package. The major differences⁴ between FEAs and CRTs are that FEAs have an array (10^8 emitters/cm²) of cold cathode electron sources (versus three thermionic electron guns) and operate at lower voltages (tens of volts versus 10 to 20 kV) and higher current densities (up to 1000 A/cm² versus 0.5 A/cm²) than CRTs.

The realization of full-color field-emitter displays (FEDs) that operate at low voltage is materials limited. Current CRT technology is based on sulfide phosphors. Sulfides degrade⁵ and emit gases that damage electron sources in high current density applications. The potential for FEA damage and limited operational lifetime makes sulfides unattractive for such applications.

Two oxides have shown promise in low-voltage applications, $\text{ZnO}:\text{Zn}$ and ZnGa_2O_4 . Reduced zinc oxide exhibits green-blue fluorescence, can be excited by electrons that have energies as low as 3 eV, possesses a luminous efficiency of 13 lm/W at 5 V, and exhibits good operational lifetime under high current densities;⁶ however, suitable chemical dopants that produce other colors and maintain low-voltage emission have not been found. Zinc gallate is a blue emitter that has a threshold voltage of 8 V and a luminous efficiency of 0.7 lm/W when the display is operated at 30 V dc.⁷

A major impediment to the development of full color FEDs is the absence of materials that show promise as low-voltage red phosphors. To provide a rational approach to the search for suitable materials, we outline the ideal properties of low-voltage phosphors: (1) low threshold voltage, (2) stability at high current densities, (3) high luminous efficiency, (4) good electron-hole

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- mobility, (5) high degree of radiative recombination of electron-hole pairs, (6) asymmetric activator ion local environment, (7) emission at desired wavelengths (colors), (8) good processability. Also, incident electrons are repelled by a negatively charged phosphor surface and this can lead to extremely low luminescent intensities at applied potentials less than about 300 V. Therefore, it is essential in low-voltage devices that the phosphor matrix and phosphor are conductive so that surface charge is removed.

In the search for low-voltage phosphors, the nature of the host, activator ions, and sensitizer ions must be considered. We have chosen materials that have anion-deficient fluorite structures as hosts and europium ions as the activators. We have examined the effect of different sensitizers on photoluminescent and low-voltage cathodoluminescent properties.

EXPERIMENTAL

Synthesis

Polycrystalline powder phosphors were synthesized from binary oxides (Aldrich) that were at least 99.99 percent (stated) pure. Reactions were performed in alumina boats at temperatures that ranged from 1100 to 1600 °C and reaction times that ranged from 16 to 120 h. The structure types of the hosts⁸ are listed below and are designated: P - pyrochlore, O - orthorhombic anion-deficient fluorite, A - A-type rare earth oxide, C - C-type rare earth oxide, and F - monoclinic distorted fluorite (space group *I*2). The compositions examined are: $\text{Y}_{1.85}\text{Eu}_{0.15}\text{Ti}_2\text{O}_7$ (P), $\text{Y}_{1.96}\text{Eu}_{0.04}\text{Sn}_2\text{O}_7$ (P), $\text{La}_{1.96}\text{Eu}_{0.04}\text{Sn}_2\text{O}_7$ (P), $\text{La}_{1.96}\text{Eu}_{0.04}\text{Zr}_2\text{O}_7$ (P), $\text{Y}_{1.96}\text{Eu}_{0.04}\text{GaSbO}_7$ (P), Eu_3NbO_7 (O), $\text{La}_{2.94}\text{Eu}_{0.06}\text{NbO}_7$ (O), $\text{La}_{1.96}\text{Eu}_{0.04}\text{ScNbO}_7$ (P), $\text{Ca}_{4/3}(\text{La}_{0.96}\text{Eu}_{0.04})\text{Nb}_{5/3}\text{O}_7$ (P), $\text{CaLa}_{0.96}\text{Eu}_{0.04}\text{TiNbO}_7$ (P), $\text{CaLa}_{0.96}\text{Eu}_{0.04}\text{SnNbO}_7$ (P), $\text{Y}_{1.96}\text{Eu}_{0.04}\text{MgWO}_7$ (P), $\text{La}_{1.96}\text{Eu}_{0.04}\text{O}_3$ (A), $\text{La}_{0.98}\text{Eu}_{0.02}\text{NbO}_4$ (F), $\text{Y}_{1.96}\text{Eu}_{0.04}\text{O}_3$ (C).

Characterization

A Scintag Diffractometer was used to collect X-ray diffraction data from 10 to 80 degrees two theta. Patterns were compared to JCPDS standards, isostructural compounds, or patterns in original references. A Horiba CAPA-700 particle size distribution analyzer was used to determine particle size distribution, and a one percent $\text{Na}_4\text{P}_2\text{O}_7$ solution in deionized water was used as a deflocculant. A Cary 5E dual beam spectrophotometer equipped with a Labsphere RSA-CA-50 hemispherical reflector and a quartz halogen lamp was used to collect reflectance data from 200 to 800 nm on polycrystalline samples. Optical bandgaps for the samples were determined from the midpoint of the absorption band in the reflectance spectrum. Fluorescence spectra were collected from 260 to 800 nm in 1 nm increments at 300 K on packed polycrystalline samples. The excitation wavelength was 253.7 nm. Data were corrected for photomultiplier tube spectral response. The collection volume and collection optics remained constant throughout the measurements. Cathodoluminescence measurements were made by the use of an evacuated system that employed a thermionic electron gun, two solenoids to focus the beam to a 1.5 mm spot, and a microammeter to monitor the current at the sample. Data were collected with a constant 200 μA emission current for anode voltages up to 1000 V. Maximum current density at the sample was about 15 mA/cm^2 . Luminance was measured with a hand held Minolta LS-100 meter equipped with close-up lens number 110 (focal length 40.5 mm). Three to ten measurements were taken and averaged for each voltage. Phosphor screens of varied thickness were prepared on 1" x 1" substrates.

RESULTS

A₂B₂O₇ crystal chemistry

Several crystal structures can be defined as anion-deficient fluorites. The type observed depends primarily on A to B cation radius ratio and the degree of oxygen deficiency. The C-type rare earth oxide structure has space group symmetry *Fm3m* (as does fluorite). The A cations are 6 coordinate and have site symmetries C_{2v} and S_6 . The A-type rare earth oxide structure has space group symmetry *P3m1*. The A cations are 7 coordinate and the maximum site symmetry is C_{3v} . One type of orthorhombic pyrochlore structure (La_3NbO_7) has space group symmetry *Cmcm*. One-third of the A cations are 8 coordinate and two-thirds are 7 coordinate and the maximum site symmetries are C_{2h} and C_{2v} . The pyrochlore structure has space group symmetry *Fd3m*. The A cations are 8 coordinate and site symmetry of the A cations is D_{3d} or lower (C_{3v}).

The A cation site symmetry is important because, in most structure types, europium occupies the A site exclusively, and the europium site symmetry influences the emission intensity from the f-f transitions. The selection rules for transitions from 5D_J multiplet to the ground-level 7F_J terms of Eu^{3+} ($4f^6$) are, according to the Russell-Saunders scheme: magnetic dipole $\Delta S = \Delta L = 0$, $\Delta J = 0, \pm 1$; electric dipole $\Delta S = 0$, $\Delta L = \pm 1$, $|\Delta L|, |\Delta J| \leq 2L$. A centrosymmetric site symmetry disallows electric-dipole transitions. The electric-dipole transitions can be significantly more intense than the magnetic-dipole transitions (e.g., $\text{Y}_2\text{O}_3:\text{Eu}$); therefore, a low symmetry activator site is desirable.

Particle Size Distribution and Optical Bandgap

The median particle size determined with respect to particle volume ranged from 7 to 11 μm for europium-doped Eu_3NbO_7 , $\text{La}_2\text{Sn}_2\text{O}_7$, $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{Y}_2\text{Sn}_2\text{O}_7$, La_2NbO_7 , $\text{La}_2\text{ScNbO}_7$, and La_2O_3 . Optical bandgaps for all fifteen samples ranged from 2.8 to 4.4 eV.

Fluorescence Spectra

Figures 1 through 3 show the europium emission spectra from the phosphors. Figure 1 shows the magnetic-dipole ($^5D_0 \rightarrow ^7F_1$) and electric-dipole ($^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_2$, $^5D_1 \rightarrow ^7F_4$) transitions for cubic pyrochlore for the samples that contain Sn, Ti, and Zr. Assignments were made based on those by Nath⁹ and McCauley and Hummel.¹⁰ The intense emission at 614 nm in $\text{Y}_{1.96}\text{Eu}_{0.04}\text{O}_3$ (Figure 3) has been assigned to the $^5D_0 \rightarrow ^7F_2$ electric-dipole transition.¹¹ The electric-dipole transitions are forbidden when europium is in a centrosymmetric environment. Thus, the intensity of these transitions is a measure of the distortion from centrosymmetry of the europium site.

Cathodoluminescence Measurements

The luminance versus anode voltage curves for europium-activated anion-deficient fluorites are compared with previously reported phosphors in Figure 4. The curves from 5 to 1000 V for the anion-deficient fluorites are displayed in Figure 5 and the curves for voltages less than 110 V are shown in Figure 6. The threshold voltages for several materials are less than 110 V: $\text{La}_2\text{Zr}_2\text{O}_7$ (100 V), reduced $\text{La}_2\text{Sn}_2\text{O}_7$ (75 V), La_2O_3 (50 V), LaNbO_4 (50V), $\text{La}_2\text{ScNbO}_7$ (40 V), $\text{Y}_2\text{Sn}_2\text{O}_7$ (20 V), and Y_2O_3 (13 V).

Figure 1. Photoluminescence spectra for europium-doped (1) $\text{Y}_2\text{Sn}_2\text{O}_7$, (2) $\text{La}_2\text{Zr}_2\text{O}_7$, (3) $\text{Y}_2\text{Ti}_2\text{O}_7$, and (4) $\text{La}_2\text{Sn}_2\text{O}_7$ under 254 nm radiation.

Figure 2. Photoluminescence spectra for doped (1) $\text{La}_2\text{ScNbO}_7$, (2) Eu_3NbO_7 , and (3) La_3NbO_7 under 254 nm radiation.

DISCUSSION

We have examined luminescence properties with similar host, same activator, and different sensitizers. We chose anion-deficient fluorites, $\text{A}_2\text{B}_2\text{O}_{8-x}$, as the host because they exhibit a variety of compositions, a wide range of conductivities, and a flexibility of sensitizer ions that can be incorporated. Europium was used because it provides intense well-known emission lines at 585, 610, and 625 nm that afford high chromatic saturation (red-orange). High valent sensitizer

Figure 3. Photoluminescence spectra for europium-doped (1) Y_2O_3 , (2) LaNbO_4 , and (3) La_2O_3 under 254 nm radiation.

Figure 4. Dependence of luminous intensity on anode voltage for ZnO:Zn and $\text{Y}_2\text{O}_2\text{S:Eu}$ (ref. 6), ZnS:Cl and ZnGa_2O_4 (ref. 7), ZnS , Y_2O_3 , and pyrochlores (this work). For comparison, the maximum brightness of a standard CRT is shown on the right.

Figure 5. Dependence of luminous intensity on anode voltage for anion-deficient fluorites.

Figure 6. Low voltage region of luminance versus anode voltage for anion-deficient fluorites. The symbols have the same identification as in Figure 5.

ions were used because they can serve as electron or hole traps and effectively mediate the transfer of electrons or holes to activator ions.

Fluorescence spectra

The integrated emission intensity of the rare earth oxides is much greater than that of the pyrochlores. Several factors can contribute to this difference; these include the identity of sensitizer, type of excitation mechanism, activator concentration, activator symmetry, radiative recombination probability, and mobility of electrons and holes.¹¹ Pyrochlores that contain the tetravalent metal ions Sn and Zr exhibit greater integrated intensities than for pyrochlores that contain Ti, Nb, Sb, and W. Intensities vary with excitation wavelength. This variation implies that different excitation mechanisms or radiative transition probabilities exist for different excitation wavelengths. The strong excitation of 254 nm (4 eV photons) was examined because the energy of the incident light is greater than the bandgap for almost all the materials.

Cathodoluminescence Properties

As shown in Figure 6, several anion-deficient fluorites display excellent low-voltage properties. The slopes of the luminance versus voltage curves (and thus the luminous efficiency) for the pyrochlores are significantly less than for previously reported materials shown in Figure 4. The excitation mechanism in all the materials is most likely direct (weak). Optimization of defect concentration can affect luminance and threshold voltage as exemplified by $\text{La}_2\text{Sn}_2\text{O}_{7-x}$. A sample heated in 99.99% pure nitrogen at 900 °C for 1 h shows a ten-fold increase in luminance at 1000 V, and the threshold voltage improves from 250 V to 75 V. The current density at the samples decreases as voltage decreases. For example, for $\text{Y}_{1.96}\text{Eu}_{0.04}\text{O}_3$ the current density is 5 mA/cm² at

300 V and is about 0.8 mA/cm² at 100 V. Nonetheless, it appears that surface bound electrons are not present in appreciable concentration at voltages as low as 13 V.

A standard cathode ray tube requires a white brightness of about 100 fL to avoid eye fatigue.¹¹ As shown in Figure 4, about 25 fL from red phosphor is required on the screen. Y_{1.96}Eu_{0.04}O₃ exhibits a luminance of 25 fL at 300 V. The luminous efficiency is 0.02 lm/W. To compete with liquid crystal displays, an efficiency of 2 to 3 lm/W is required for a red phosphor. It should be possible to engineer improvements in luminous efficiency through optimization of activator concentration and particle size distribution and through improvements in screen fabrication processes.

CONCLUSIONS

Through judicious choice of host and sensitizer along with appropriate screen fabrication, we achieve excellent threshold voltages in anion-deficient fluorites. The relative intensity of a sample under irradiation of 254 nm photons is a good indicator of the relative luminosity under irradiation of electrons in the limited number of samples considered. In the limited group of sensitizers examined in this study, materials that contain yttrium have a more intense luminescence response than those with lanthanum (Y₂O₃ versus La₂O₃ and Y₂Sn₂O₇ versus La₂Sn₂O₇), and pyrochlores that contain tin, zirconium, and niobium have a more intense response than those with tungsten, antimony, and titanium. Finally, a full-color field-emitter array that has white brightness of a standard CRT could be fabricated with ZnO:Zn, ZnGa₂O₄, and Y₂O₃:Eu and operated at 300 V.

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