Luminescent impurity doping trends in alternating-current thin-film electroluminescent phosphors

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Abstract

The doping properties of three alternating-current thin-film electroluminescent (ACTFEL) phosphor host / luminescent impurity systems, ZnS:Mn, SrS:Ce, and SrS:Cu, are elucidated, and the ACTFEL device implications of these properties are assessed. Mn is isovalent, Ce is a donor, and Cu is an acceptor. Moreover, Ce is readily ionized in SrS, so that it behaves as a double donor. The distinctly different doping nature of these three luminescent impurities leads to dramatically disparate defect and device physics trends. The donor / acceptor nature of Ce / Cu in SrS results in charge neutrality being achieved in SrS:Ce and SrS:Cu via self-compensation-induced vacancy creation; subsequent defect complexing between oppositely charged luminescent impurities and self-compensation-induced vacancies results in more complex ACTFEL device behaviors such as dynamic space charge, trailing-edge emission, charge
collapse, color tuning, and electroluminescence (EL) thermal quenching. In contrast, the iso-
valent nature of ZnS:Mn leads to more ideal ACTFEL device operation. This suggests that the
optimal ACTFEL phosphor luminescent impurity is isovalent.
1 Introduction

The development of full-color alternating-current thin-film electroluminescent (ACTFEL) flat-panel displays has motivated researchers to explore a variety of phosphor host / luminescent impurity combinations. [1, 2] Sulfides or sulfur anion based compounds, e.g., thiogallates, have been the primary ACTFEL phosphors, although it has recently been contended that oxides constitute a viable alternative for ACTFEL phosphor applications. [3]

Three ACTFEL phosphor host / luminescent impurity combinations that have elicited the most research and development attention are ZnS:Mn, SrS:Ce, and SrS:Cu. ZnS and SrS are the two most common commercial ACTFEL phosphor hosts, so it is not surprising that the three most studied ACTFEL systems would utilize these phosphors. Rather, it is the radically different dopant nature of these three luminescent impurities, Mn, Ce, and Cu that is the motivation for writing this paper. All three are substitutional impurities on cation sites, i.e. Zn or Sr. However, using the terminology of semiconductor physics, [4] Mn is isovalent, having the same valence as the host cation, i.e., Mn$^{2+}$ on a Zn$^{2+}$ site; Ce is a donor, having a valence greater than the host cation, i.e., Ce$^{3+}$ on a Sr$^{2+}$ site; and Cu is an acceptor, having a valence less than the host cation, i.e., Cu$^{1+}$ on a Sr$^{2+}$ site.

The goal of this paper is to explore the implications and ramifications of employing different types of substitutional dopants as luminescent impurities in ACTFEL phosphors. It is shown that the dopant nature of the luminescent impurity can affect many aspects of ACTFEL behavior such as charge neutrality, self-compensation, defect creation and association, static / dynamic space charge creation and annihilation, trailing-edge emission, color tuning, and electroluminescence (EL) thermal quenching.
2 Luminescent impurity dopant trends

2.1 Isovalent substitutional impurities: ZnS:Mn

Figure 1 displays the approximate ionization energy locations for Mn in ZnS, as well as Ce in SrS, and Cu in SrS, which are discussed in Secs. 2.2 and 2.3 of this paper. [The upper (lower) charge state indicated for each energy level shown in Fig. 1 indicates the charge state of the energy level if it is filled (not filled) with an electron.] Mn\textsubscript{Zn} is an example of an isovalent substitutional luminescent impurity which, if ionized, behaves as a single donor, whose charge state characteristics are indicated in Fig. 1. Further discussion is required to clarify the meaning and implications of this luminescent impurity classification scheme.

There are two basic approaches for discussing the charge state characteristics of luminescent impurity substitutional dopants in phosphors, the chemical and the physical approach. It is important to recognize that these approaches are useful for distinctly different types of assessment. To avoid confusion, it is best to exclusively employ the chemical approach when treating bonding issues and the physical approach when assessing electronic issues and to never use a hybrid approach in which both are utilized concurrently.

The chemical approach focuses on bonding issues, implicitly assuming that ionic bonding dominates and that the charge of an atom is given by its oxidation state. [5] In chemical language, the oxidation states of the Mn substitutional luminescent impurity and the Zn phosphor cation are identical so that a Mn\textsuperscript{2+} ion sits on a Zn\textsuperscript{2+} site. The chemical bonding properties of Mn and Zn are expected to be similar since they have a common ionization state and, hence valence.

In contrast, the physical approach focuses on electronic issues. [4] Differences in oxidation state or valence between the luminescent impurity and substitutional cation are of primary consideration. In this regard, Mn is isovalent with respect to Zn, which means that the Mn substitutional impurity
has the same valence or ionization state as the host cation. Thus, a Mn\textsubscript{Zn} luminescent impurity is expected to be electrically neutral in a ZnS lattice in equilibrium (as well as under normal ACTFEL operation, as discussed below). This neutral charge state is indicated in Fig. 1 by a 0 above the Mn\textsubscript{Zn} energy level. If a Mn\textsubscript{Zn} luminescent impurity electronic state becomes ionized by losing its electron to the conduction band, for example, this electronic state becomes positively charged, as indicated by the + sign shown below the Mn\textsubscript{Zn} energy level in Fig. 1. Two-photon absorption experiments have been used to estimate the Mn\textsubscript{Zn} ionization energy as approximately 0.9 eV below the top of the valence band [6], whereas x-ray photoelectron spectroscopy and synchrotron radiation measurements provide estimates of 3 eV and 3.5 eV below the valence band maximum, respectively. [7, 8] Note that this ionization energy level corresponds to the ground state position of the Mn luminescent impurity. Since the ionization energy of Mn\textsubscript{Zn} with respect to the conduction band minimum is very large, it is unlikely that it will ever be ionized under normal ACTFEL operation.

Subsequent discussion will show that since Mn\textsubscript{Zn} is isovalent and possesses a very large ionization energy, it behaves in an ideal manner as a luminescent impurity compared to Ce\textsubscript{Sr} and Cu\textsubscript{Sr}.

### 2.2 Substitutional donor impurities: SrS:Ce

Figure 1 displays the approximate ionization energy locations for Ce in SrS. In chemical language, the oxidation states of the Ce substitutional luminescent impurity and the phosphor Sr cation differ, so that a Ce\textsuperscript{3+} ion sits on a Sr\textsuperscript{2+} site. From a physical perspective, this oxidation state mismatch means that Ce enters the SrS lattice as a donor which is single positively charged in equilibrium, but could be neutral if the donor ionization state is filled with an electron; this situation corresponds to the first ionization state of Ce\textsubscript{Sr}, as shown in Fig. 1. As is well known, [9, 10] SrS:Ce ACTFEL operation involves ionization of Ce from its ground state to the conduction band. This Ce ionization
is usually attributed to resonant tunneling from the Ce excited state into the conduction band. For such an ionization process to occur at an appreciable rate, the Ce excited state and the conduction band minimum must have similar energies. This implies that the Ce ground state is located \(\sim 2.5-3.0\) eV below the SrS conduction band minimum, as crudely indicated in Fig. 1. Since Ce enters the SrS lattice as a single positively charged donor, ionization of a Ce luminescent impurity corresponds to the second ionization of a double donor into a ++ charge state, as shown in Fig. 1. In chemical language, the Ce is now in a formal +4 oxidation state.

Now that the second donor ionization energy of Ce\(_{Sr}\) has been estimated, it can be pointed out that the Ce\(_{Sr}\) first donor ionization energy should be more shallow (i.e. closer to the conduction band) than the second ionization state. Therefore, the first ionization energy of Ce\(_{Sr}\) is expected to be in the upper portion of the energy gap towards the conduction band minimum, as shown in Fig. 1; it is possible, but unlikely, that this first ionization energy is degenerate with the conduction band, i.e., positioned above the conduction band minimum. Evidence that the first ionization energy of Ce\(_{Sr}\) is indeed in the upper portion of the bandgap is presented in Sec. 3.2 of this paper.

The fact that Ce is a substitutional double donor in SrS has a multiplicity of ACTFEL phosphor defect chemistry implications as discussed in the following paragraphs, as well as ACTFEL device physics implications, as discussed in Sec. 3.2 of this paper.

First, consider the expected equilibrium Fermi level position and how this determines the charge state of luminescent impurities and defects present in the phosphor. All high-quality ACTFEL phosphors are insulating and operate via electron injection / transport. These two requirements imply that the equilibrium Fermi level is at least 0.7 eV below the conduction band maximum (to insure that the phosphor is insulating) but above mid-gap (to insure that electron injection dominates). Bringuier estimated the equilibrium Fermi level for ZnS:Mn to be \(\sim 0.9\) eV below the conduction band minimum, [11] which is probably typical of a well behaved ACTFEL phosphor.
Thus, the equilibrium Fermi level position for all high-quality ACTFEL phosphors is expected to be $\sim 0.7 \text{ eV} \leq E_C - E_F \leq \sim 2.0 \text{ eV}$, i.e., midgap. This equilibrium Fermi level position establishes the quiescent charge state of all of the luminescent impurities and defects present in the phosphor; to first order, all of the electronic states above (below) the Fermi level are empty (filled). Thus, to first order, all acceptor states are expected to be ionized, i.e., negatively charged and all donor states more shallow than about $\sim 0.7 \text{ eV}$ are expected to be ionized, i.e. positively charged.

Second, consider charge neutrality. For an insulating phosphor to be charge neutral, the total amount of positive and negative charge associated with luminescent impurities and defects must sum to zero. In SrS:Ce, there are $\sim 10^{19} \text{ cm}^{-3}$ ionized Ce atoms. Thus, in order to achieve charge neutrality, an equal concentration of negative defect charge is required. Electron paramagnetic resonance (EPR) studies demonstrate that this compensating charge arises from single negatively charged Ce luminescent impurity - strontium vacancy defect complexes, i.e., $(\text{Ce}_{\text{Sr}}\text{-}V_{\text{Sr}})^-$; isolated Ce$_{\text{Sr}}$ is a donor and isolated V$_{\text{Sr}}$ is a double acceptor. Given the expected position of the Fermi level, the defect complex is a single negatively charged acceptor. [12, 13, 14]

Ce$_{\text{Sr}}$-V$_{\text{Sr}}$ defect complexes are believed to form as a consequence of self-compensation, [15, 16] as explained in the following. Consider an idealized situation in which the phosphor, SrS in the case addressed here, is initially intrinsic, which means that its Fermi level is positioned near the middle of the bandgap with the phosphor having a negligible concentration of defects and impurities. Now assume that the phosphor is doped with an increasing concentration of donors; this increasing donor concentration results in a modulation of the Fermi level towards the conduction band. Self-compensation is envisaged to arise when the Fermi level position reaches a critical energy, $E_{F}^\text{crit}$, at which it is more energetically favorable to create an intrinsic, self-compensating acceptor defect than to continue to modulate the Fermi level towards the conduction band. [17, 18] Although other types of intrinsic defects are possible, energetic considerations suggest that self-compensation
is most likely mediated via vacancy creation, at least for ZnS and SrS, as indicated in Table I. [16, 19, 20]

An estimate of $E_F^{\text{crit}}$ for donor doping in SrS may be obtained by recognizing that $E_F^{\text{crit}}$ is established by the condition that the enthalpy of formation of a strontium vacancy is equal to zero,

$$\Delta H_f(V_{\text{Sr}}^{-2}) = \Delta H_f(V_{\text{Sr}}^x) + (E_{A1} - E_F) + (E_{A2} - E_F) = 0,$$

where $\Delta H_f(V_{\text{Sr}}^{-2})$ and $\Delta H_f(V_{\text{Sr}}^x)$ refer to the enthalpy of formation of a doubly ionized and neutral cation vacancy and $E_{A1}$ and $E_{A2}$ refer to the first and second ionization energies (using the top of the valence band as the energy reference) of the cation vacancy. Solving for the Fermi level in Eq. 1 results in

$$E_F^{\text{crit}} = \frac{1}{2} \left[ \Delta H_f(V_{\text{Sr}}^x) + E_{A1} + E_{A2} \right].$$

Substituting 4.1 eV into Eq. 2 for the enthalpy of formation of the neutral cation vacancy [20] and assuming $E_{A1} \sim 0.1$ eV and $E_{A2} \sim 1.0$ eV (identical to ionization energy estimates for a zinc vacancy in ZnS [15]), yields $E_F^{\text{crit}} \sim 2.6$ eV. Since the bandgap of SrS is approximately 4.3 eV, this assessment indicates that when the Fermi level is within $\sim 1.7$ eV from the conduction band minimum, it is more energetically favorable to create self-compensating $V_{\text{Sr}}$'s than to modulate the Fermi level closer to the conduction band. Although this calculation is rather crude, since the $V_{\text{Sr}}$ ionization energies are not known, as long as these ionization energies lie within the bottom third of the bandgap the energetics of self-compensation via cation vacancy creation appear to be favorable when the Fermi level approaches the conduction band.

Self-compensation-induced defects, $V_{\text{Sr}}$, double acceptors in the case of SrS:Ce, tend to associate, or form complexes with oppositely charged luminescent impurities, since the coulombic energy of association lowers the free energy. [15] The binding energy of such a defect complex is often estimated using the fully screened (i.e., employing the low frequency dielectric constant) point
charge coulombic energy

$$\Delta E_{\text{binding}} = \frac{Z_1 Z_2 q^2}{4\pi \varepsilon r_{12}},$$

where $Z_1$ and $Z_2$ are the charges of the respective point defects being considered, $r_{12}$ is the distance between point defects, and $\varepsilon$ is the low frequency dielectric constant (9.4 for SrS [20]). Since the defects constituting the complex $\text{Ce}_{\text{Sr}} - V_{\text{Sr}}$ sit on second nearest neighbor sites (a distance of 0.43 nm), $\Delta E_{\text{binding}} \sim 0.7$ eV. Thus, if a $V_{\text{Sr}}$ is created by self-compensation, there is a strong driving force for it to associate with a $\text{Ce}_{\text{Sr}}$ luminescent impurity to form a $\text{Ce}_{\text{Sr}} - V_{\text{Sr}}$ defect complex so that it can lower its energy by this significant amount of coulombic binding energy. [Anticipating ahead to Sec. 2.3, note that the constituents of the $\text{Cu}_{\text{Sr}} - V_{\text{S}}$ defect complex sit on nearest neighbor sites (a distance of 0.3 nm) so that the binding energy is even larger in this case, $\Delta E_{\text{binding}} \sim 1.0$ eV.]

An additional aspect of associated defect complexes such as $\text{Ce}_{\text{Sr}} - V_{\text{Sr}}$ is that they have ionization energies which differ from those of isolated point defects. [15] According to Kröger, association results in the ionization energies of the defect complex constituents becoming more shallow or even being completely removed out of the bandgap. For example, Fig. 2 illustrates expected trends for an associated $\text{Ce}_{\text{Sr}} - V_{\text{Sr}}$ defect complex compared to isolated $\text{Ce}_{\text{Sr}}$ and $V_{\text{Sr}}$ point defects. Kröger asserts that the total variation of the ionization energy positions due to association is approximately equal to $\Delta E_{\text{binding}}$ (i.e. $\sim$0.7 eV for the case of a $\text{Ce}_{\text{Sr}} - V_{\text{Sr}}$ defect complex).

### 2.3 Substitutional acceptor impurities: SrS:Cu

Figure 1 displays the approximate ionization energy locations for Cu in SrS. In chemical language, the oxidation states of the Cu substitutional luminescent impurity and the phosphor Sr cation differ, so that a $\text{Cu}^{1+}$ ion sits on a $\text{Sr}^{2+}$ site. From a physical perspective, this oxidation state mismatch means that Cu enters the SrS lattice as an acceptor which is single negatively charged
in equilibrium, but would be neutral with hole trapping. The Cu ionization energy is positioned in the lower part of the bandgap in Fig. 1, as is the usual case for acceptor dopants.

Since Cu is an acceptor dopant in SrS, the equilibrium Fermi level would, incorrectly we believe, be expected to be located below the middle of the bandgap. However, there are compelling reasons to believe that the equilibrium energy band situation is not as simple as the flat-band picture shown in Fig. 3a. This energy band diagram implies that a SrS:Cu ACTFEL device should operate via hole injection and transport, since the interface and bulk hole injection barriers are much smaller than corresponding electron injection barriers.

However, this appears to be highly unlikely since photo-induced transferred charge (PIQ) and photo-induced luminescence (PIL) measurements performed by several groups demonstrate that hole transport is very poor in SrS ACTFEL devices doped with Ce or Cu luminescent impurities. [21, 22, 23, 24, 25, 26] PIQ / PIL measurements involve photo-excitation of electron-hole pairs in the phosphor near one of the phosphor/insulator interfaces, transport of this photo-induced charge across the phosphor (aided by the application of a DC voltage across the ACTFEL stack), and measurement of the charge transferred across the phosphor layer or the luminescence emitted from the phosphor layer, as a function of the magnitude of the applied DC voltage. Electron and hole PIQ curves are shown in Fig. 4 for a sputter deposited SrS:Cu ACTFEL device with a phosphor thickness of 1100 nm. [26] Note that there is an appreciable electron PIQ signal over the entire range of maximum applied voltage, with an electron multiplication threshold at ~110-130 V (i.e. ~1 MV/cm); this curve illustrates the excellent transport properties of electrons in SrS:Cu. In contrast, there is no discernible hole PIQ signal even for phosphor fields in excess of ~1.5 MV/cm; thus, strong hole trapping occurs within the SrS:Cu phosphor layer.

Therefore, to rationalize efficient SrS:Cu ACTFEL device operation, which appears to require electron injection / transport, and p-type Cu doping, the equilibrium energy band diagram shown
in Fig. 3b is proposed. This energy band picture postulates interfacial Fermi-level pinning which positions the interface Fermi level in the upper portion of the energy bandgap, as required for electron-injection, and yet allows the bulk Fermi level to be located below midgap, a likely situation given a Cu acceptor concentration of $\sim 10^{19}$ cm$^{-3}$. A consequence of this picture, however, is the existence of negative space charge in the phosphor under equilibrium conditions.

As an alternative to Fig. 3b, another possible way to rationalize electron injection / transport in SrS:Cu ACTFEL devices even though they are heavily p-doped is to assert that the self-compensation energetics are such that the $E_F^{crit}$ occurs in the upper portion of the bandgap. For SrS:Cu, the expected defect complex for vacancy-mediated self-compensation is $(Cu_{Sr}-V_S)^+$. For this case, $E_F^{crit}$ is established by the condition that the enthalpy of formation of a sulfur vacancy is equal to zero,

$$\Delta H_f(V_S^{+2}) = \Delta H_f(V_S^x) + (E_F - E_{D1}) + (E_F - E_{D2}) = 0, \tag{4}$$

where $E_{D1}$ and $E_{D2}$ refer to the first and second ionization energies (using the top of the valence band as the energy reference) of the anion vacancy. Solving for the Fermi level in Eq. 4 results in

$$E_F^{crit} = \frac{1}{2} [E_{D1} + E_{D2} - \Delta H_f(V_S^x)]. \tag{5}$$

Substituting 2.9 eV into Eq. 5 for the enthalpy of formation of the neutral anion vacancy, [20] assuming $E_{D1} \sim 0.71$ eV, [27], and estimating $E_{D2} \sim 1.7$ eV (i.e. assuming that the second ionization energy is about 1 eV larger than the first ionization energy; this estimate is very crude and arises from recognizing that a second ionization involves overcoming a coulombically attractive energy barrier associated with the ionizing electron and the positively charged ion; the coulombic attraction is evaluated at a nearest neighbor distance), yields $E_F^{crit} \sim 1$ eV. Thus, this calculation suggests $E_F^{crit}$ to be below midgap. This estimate, while very crude due to ionization energy uncertainties, suggests that the electron injection / transport behavior of SrS:Cu ACTFEL devices
more likely arises as a consequence of Fermi-level interface pinning than from the energetics of self-compensation.

2.4 Luminescent impurity dopant trend summary

The first four columns of Table II summarize important aspects of the preceding luminescent impurity doping trend discussion. The fact that Mn is isovalent in ZnS means that no compensating defect is required to achieve charge neutrality. In contrast, the donor- and acceptor-like nature of Ce and Cu, respectively, in SrS mandates the formation of self-compensation-induced vacancies which, when associated with oppositely charged luminescent impurities, results in the formation of \((\text{Ce}_{S_{r}}-\text{V}_{S_{p}})^{-}\) or \((\text{Cu}_{S_{r}}-\text{V}_{S})^{+}\) defect complexes. As discussed in Sec. 3 of this paper, differences in the dopant nature of the luminescent impurity employed can manifest themselves differently in the operation of an ACTFEL device.

3 Luminescent impurity dopant device implications

This section is devoted to a discussion of device implications related to the dopant nature of the luminescent impurity utilized in the ACTFEL phosphor. Since the primary objective is to correlate luminescent impurity dopant properties to ACTFEL device performance, this presentation is rather terse, primarily presenting conclusions from other work. Details of this work may be found in the references cited.

The presence and nature of positive space charge in the phosphor region of an ACTFEL device is of fundamental importance in determining ACTFEL operation. [28, 29] Space charge may be classified as either static or dynamic. Dynamic space charge denotes positive charge in the phosphor which is at least partially created and annihilated during each period of the bipolar voltage waveform used to drive the ACTFEL device. Static space charge is envisaged as positive space charge that
is present in the phosphor during steady-state operation of the ACTFEL device and whose density and distribution does not change appreciably during steady-state operation.

A complete description of ACTFEL positive space charge requires identifying both creation and annihilation mechanisms. Figure 5 illustrates the three possible mechanisms of positive space charge generation: field emission, i.e., this designation refers to electron emission from a trap by thermionic emission, tunneling, or phonon-assisted tunneling; trap-to-band impact ionization; and band-to-band impact ionization with hole trapping. Figure 6 illustrates the two mechanisms of space charge annihilation: electron emission / recombination and hole emission. Note that space charge creation and annihilation sometimes involves luminescent impurities. For example, space charge annihilation involving a luminescent impurity via electron emission / radiative recombination is an alternative to impact excitation as an electroluminescence mechanism.

Given the differing dopant nature of ZnS:Mn, SrS:Ce, and SrS:Cu ACTFEL phosphors, it is not surprising that the space charge properties, as well as the luminescent impurity electroluminescence mechanisms, of these phosphors are also distinctly different. Each of these three phosphors are now considered individually.

3.1 ZnS:Mn

ZnS:Mn ACTFEL device operation is strongly affected by static space charge, even though static space charge is more difficult to experimentally detect than dynamic space charge. [28] The most direct and convincing evidence for static space charge is the existence of transferred charge capacitance overshoot in conjunction with the absence of overshoot in normal capacitance-voltage characteristics. [30] The static space charge density is estimated as \( \sim 7 \times 10^{16} \text{ cm}^{-3} \). [28] Static space charge formation is most successfully modeled as being created by band-to-band impact ionization and hole trapping into a deep hole trap. [29] The large capture cross section for this deep
hole trap (~7 × 10^{-13} \text{ cm}^2, as estimated from PIQ measurements [31], implying a coulombically attractive capture process) suggests that this trap is likely a defect complex involving a zinc vacancy. The ZnS:Mn electroluminescence mechanism is identified as impact excitation. [32]

Typically, trailing edge emission (TEE) is not observed in ZnS:Mn ACTFEL devices. [33] However for certain types of ZnS:Mn ACTFEL devices, e.g., those grown by atomic layer epitaxy (ALE) using a chlorine-containing precursor gas, a weak TEE is observed. [34, 35] Usually, TEE is strong evidence for the existence of positive space charge in the phosphor, most likely associated with self-compensation-induced Cl_{z-V_{Zn}} defect complexes for the case of ALE(Cl) ZnS:Mn (this identification arises from the presence of blue TEE, which is ascribed to self-activated donor-acceptor emission [35]). TEE in ZnS:Mn is usually attributed to the back-injection of electrons from anode interface states and impact excitation of Mn in the high field region near the anode when the applied voltage is removed. [36, 37] For this type of TEE, the role of positive space charge is to bend the energy bands so that electron back-injection can occur. TEE has also been detected in thick dielectric ZnS:Mn EL devices at large over-voltages (greater than ~65 V). [33] These devices do not appear to possess appreciable amounts of positive space charge. This type of TEE is unusual because under normal operation the phosphor field is not large enough for back injection / impact excitation to occur at the end of an applied voltage pulse. However, these thick dielectric EL devices allow for the transfer of more charge and, hence, higher operating electric fields. Thus, TEE arises as a simple consequence of operating the EL device in a manner in which the polarization field builds up sufficiently so that back injection / Mn impact excitation are possible. In summary, although TEE is usually strong evidence for the presence of positive space charge in the phosphor, it is also possible to observe TEE under non-standard operating conditions in which the polarization field is anomalously large.
3.2 SrS:Ce

Dynamic space charge plays an important role in SrS:Ce ACTFEL device operation. [29, 38, 39, 40, 41, 42, 43, 44] Dynamic space charge creation is ascribed to the ionization of Ce luminescent impurities and other deeper levels. [43] Simulation suggests that the SrS:Ce positive space charge creation mechanism is trap-to-band impact ionization. [29] Dopant considerations discussed previously in this paper suggest that Ce$_{Sr}$ and Ce$_{Sr}$-V$_{Sr}$ are the most likely ionization candidates which give rise to dynamic space charge. Experiments conducted using laser excitation during ACTFEL operation indicate that the Ce$^{+3}$ excited state is more than 0.23 eV below the conduction band minimum and that the ionization energy of the deep level defect is greater than 3.6 eV below the conduction band minimum, i.e., less than $\sim$0.7 eV from the valence band maximum. [43] It is likely that this ionized deep level corresponds to the second acceptor ionization energy of the Ce$_{Sr}$-V$_{Sr}$ self-compensation-induced defect complex. The fact that this ionization energy is relatively shallow is likely due to an association-induced perturbation of the V$_{Sr}$ ionization energy, as indicated in Fig. 2.

TEE is omnipresent in SrS:Ce ACTFEL devices. The TEE emission peak is sometimes larger than the leading edge emission peak. Note that positive space charge plays dual roles in this SrS:Ce TEE process; first, it bends the energy bands so that electron back-injection can occur and second, it acts as the recombination site. If Ce$_{Sr}$ and Ce$_{Sr}$-V$_{Sr}$ are assumed to be the source of space charge in the SrS:Ce phosphor, radiative recombination would be much more probable at a Ce$_{Sr}$ site, whose charge state is $\text{+++}$ when ionized, compared to a Ce$_{Sr}$-V$_{Sr}$ site, which is neutral when ionized. This tendency arises from the coulombic nature of the radiative recombination process for these two types of defects. A coulombically attractive trap typically has a capture cross-section greater than $\sim 10^{-14}\text{cm}^2$, whereas a neutral trap has a capture cross-section of $\sim 10^{-14}-10^{-18}\text{cm}^2$. [45]
Since TEE is so pervasive in SrS:Ce ACTFEL devices, it is evident that the impact ionization / radiative recombination electroluminescence mechanism plays an important role in the operation of such devices. Whether or not Ce impact excitation is an important electroluminescence mechanism is less clear. It has been asserted that impact excitation is a more efficient process than impact ionization / radiative recombination. [43] Given the defect association-induced ionization energy trends illustrated in Fig. 2, impact excitation would be more likely for isolated Ce$_{Sr}$ luminescent impurities than for Ce$_{Sr}$-V$_{Sr}$ complexes since the Ce$_{Sr}$ ground state is further below the conduction band minimum, and, thus, more difficult to ionize. This also implies that impact ionization would be more probable for Ce$_{Sr}$-V$_{Sr}$ complexes, since less energy is required to ionize the Ce ground state when Ce is a constituent of a Ce$_{Sr}$-V$_{Sr}$ complex.

Several characteristics of SrS:Ce ACTFEL devices provide evidence that the first ionization energy of Ce is located near the conduction band.

First, consider the maximum transferred charge - maximum applied voltage ($Q_{max}$-$V_{max}$) curves obtained at three different frequencies for a SrS:Ce ACTFEL device, as shown in Fig. 7. The step in $Q_{max}$ above threshold is associated with space charge creation. Above the $Q_{max}$ step, the $Q_{max}$-$V_{max}$ slope is approximately equal to the insulator capacitance of the ACTFEL device. Pre-threshold charge transfer is distinctly evident in Fig. 7. Simulation shows that this pre-threshold charge trend is consistent with a bulk donor trap in the phosphor. [46] Thus, the first ionization state of an isolated Ce$_{Sr}$ donor appears to be a likely identification for this trap.

Second, Fig. 8 shows an internal charge - phosphor field ($Q$-$F_P$) curve for a SrS:Ce ACTFEL device obtained at 40 V above threshold. The decrease in charge during the trailing edge portion of the positive applied voltage pulse (and to a lesser extent, the negative pulse) is denoted 'charge collapse'. Charge collapse is attributed to the back injection of electrons trapped in shallow states (or possibly conduction band states) near the anode phosphor / insulator interface. Charge collapse
is observed in most SrS:Ce ACTFEL devices, but is typically not seen in other types of SrS devices, e.g., SrS:Cu and SrS:Cu,Ag. [44] Thus, it seems likely that charge collapse is associated with the first donor ionization energy of a Ce$_{Sr}$-V$_{Sr}$ complex. We prefer to ascribe charge collapse to the first ionization energy of a Ce$_{Sr}$-V$_{Sr}$ complex rather than an isolated Ce$_{Sr}$ luminescent impurity because association results in a more shallow ionization energy.

Third, temperature-dependent subthreshold voltage-induced transferred charge (VIQ) measurements, an example of which is shown in Fig. 9, provide evidence for the existence of a shallow, i.e., ~0.1 eV donor trap in SrS:Ce ACTFEL devices. [26] This shallow trap is again ascribed to the first ionization energy of a Ce$_{Sr}$-V$_{Sr}$ complex for the same reason as given in the previous paragraph.

3.3 SrS:Cu

SrS:Cu ACTFEL device operation is also strongly affected by dynamic space charge. [44, 47] Evidence for dynamic space charge includes capacitance-voltage and Q-F$_P$ overshoot [44] as well as TEE. [47] Given differences in the dopant nature of Ce and Cu, it is hardly surprising that the space charge creation and annihilation mechanisms should differ for these luminescent impurities.

Space charge creation in a SrS:Cu ACTFEL device is attributed to band-to-band impact ionization and hole trapping at a Cu$_{Sr}$ or a Cu$_{Sr}$-V$_{S}$ acceptor-like center. [46, 48] Space charge annihilation is due to both electron injection / radiative recombination and hole emission at an ionized Cu$_{Sr}$ or Cu$_{Sr}$-V$_{S}$ acceptor-like center; when electrons are back-injected at the end of an applied voltage pulse, radiative recombination results in TEE. At elevated temperatures, space charge annihilation via hole emission from ionized Cu$_{Sr}$ or Cu$_{Sr}$-V$_{S}$ acceptor-like centers increases, thus giving rise to a dramatic increase in the device threshold voltage and decrease in the luminance. This temperature-dependent degradation in the ACTFEL performance is denoted EL thermal quenching, [48] and constitutes an important technical challenge that has recently received attention. [49]
Color tuning is another aspect of SrS:Cu phosphor behavior that directly depends on the dopant nature of Cu. [50, 51] The basic idea of color tuning in the SrS:Cu phosphor system is that the electroluminescence color may be tuned from blue to green with the addition of appropriate codopants. To obtain blue emission, donors such as chlorine are used as codopants. Donors suppress the formation of sulfur vacancies so that Cu luminescent impurities sit predominantly on sixfold coordinated lattice sites, which provide blue emission; in this case, extrinsic compensation is employed to circumvent self-compensation. In contrast, green emission is obtained by using acceptor codopants such as Na. Acceptor doping enhances the formation of sulfur vacancies, which then associate with Cu luminescent impurities. These fivefold coordinated Cu$_{Sr}$-V$_{S}$ defect complexes yield green emission; in this case, self-compensation is induced and exploited. Thus, self-compensation is used as a materials engineering tool for color tuning.

3.4 Summary

The last two columns of Table II summarize important ACTFEL device behavior that arise as a consequence of the dopant nature of the luminescent impurity employed. Perhaps the most striking aspect of this table is that isovalent behavior is rather benign whereas donor / acceptor behavior is quite dramatic with respect to ACTFEL device operation consequences.

When an isovalent luminescent impurity is utilized, the device consequences of this luminescent impurity dopant choice are modest. The only ZnS:Mn entry in the last two columns of Table II is ‘static space charge’. We believe that the deep acceptor state that gives rise to static space charge is most likely a self-compensation-induced V$_{Zn}$ complex arising as a consequence of the fact that the equilibrium position of the ZnS Fermi level is invariably above E$_{F}^{\text{crit}}$. Presumably, the ZnS equilibrium Fermi level position is established by the stoichiometry of the ZnS film and the donor / acceptor properties of unintentionally incorporated residual impurities. The important point here
is that the driving force for this non-ideal behavior, i.e., static space charge in this case, is rather weak since the intrinsic defect / residual impurity concentration is expected to be relatively small,\n\[\sim 10^{16}-10^{17} \text{ cm}^{-3}.\]

In contrast, when the luminescent impurity is a donor or acceptor, there is strong driving force for non-ideal behavior since the expected luminescent impurity concentration is \[\sim 10^{19}-10^{20} \text{ cm}^{-3}.\] Such a large donor or acceptor concentration strongly perturbs space charge neutrality, leading a wide bandgap phosphor to resort to self-compensation, and thus introducing new electronic states into the bandgap which are associated with luminescent impurities, self-compensation-induced vacancies, codopants, and associated defect complexes thereof. These electronic states lead to a multiplicity of ACTFEL device operation consequences, some of which are enumerated in Table II.

4 CONCLUSIONS

The dopant properties of ZnS:Mn, SrS:Ce, and SrS:Cu ACTFEL phosphors are discussed. Mn is isovalent, Ce is a double donor, and Cu is a single acceptor. The differing dopant nature of these three luminescent impurities leads to radically different defect and device physics trends, as summarized in Table II.

The isovalent nature of ZnS:Mn results in relatively ideal ZnS:Mn ACTFEL device operation, except for the presence of static space charge. In retrospect, it is not surprising that the use of an isovalent luminescent impurity leads to nearly ideal behavior since few electronic states are expected within the bandgap, arising from a relatively low concentration of intrinsic defects and residual impurities.

In contrast, the donor (acceptor) nature Ce (Cu) in SrS results in many different kinds of non-ideal ACTFEL device behaviors, i.e., dynamic space charge, trailing-edge emission, and charge collapse for SrS:Ce; dynamic space charge, trailing-edge emission, color tuning, and EL thermal
quenching for SrS:Cu. The driving force for this non-ideal ACTFEL behavior is the high luminescent impurity doping concentration which leads to the introduction of many new electronic charge states into the bandgap.

ACKNOWLEDGMENTS

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References


Table I: Estimated intrinsic point defect energies for ZnS [16, 19] and SrS. [20]

The defect dopant nature is assessed using Kröger’s rules. [15]

<table>
<thead>
<tr>
<th>Defect Type</th>
<th>Defect Dopant Nature</th>
<th>ZnS (eV)</th>
<th>SrS (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation vacancy</td>
<td>Double acceptor</td>
<td>2.9</td>
<td>4.1</td>
</tr>
<tr>
<td>Anion vacancy</td>
<td>Double donor</td>
<td>2.5</td>
<td>2.9</td>
</tr>
<tr>
<td>Cation interstitial</td>
<td>Double donor</td>
<td>11.8</td>
<td>9.6</td>
</tr>
<tr>
<td>Anion interstitial</td>
<td>Double acceptor</td>
<td>19.6</td>
<td>14.2</td>
</tr>
<tr>
<td>Anion-on-cation antisite</td>
<td>Quadruple donor</td>
<td>9.3</td>
<td>18.5</td>
</tr>
<tr>
<td>Cation-on-anion antisite</td>
<td>Quadruple acceptor</td>
<td>9.5</td>
<td>14.9</td>
</tr>
</tbody>
</table>
Table II: Luminescent impurity dopant trend summary. (tbii = trap-to-band impact ionization, biii = band-to-band impact ionization)

<table>
<thead>
<tr>
<th>Phosphor: luminescent impurity</th>
<th>Dopant type</th>
<th>Compensating defect</th>
<th>Associated defect complex / binding energy</th>
<th>Dynamic space charge creation mechanism</th>
<th>Other trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS:Mn</td>
<td>isovalent</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>static space charge</td>
</tr>
<tr>
<td>SrS:Ce (double)</td>
<td>donor</td>
<td>$V_{Sr}$</td>
<td>$(Ce_{Sr}-V_{Sr})^-$</td>
<td>tbii</td>
<td>dynamic space charge trailing edge emission charge collapse</td>
</tr>
<tr>
<td>SrS:Cu (single)</td>
<td>acceptor</td>
<td>$V_S$</td>
<td>$(Cu_{Sr}-V_S)^+$</td>
<td>biii</td>
<td>dynamic space charge trailing edge emission color tuning EL thermal quenching</td>
</tr>
</tbody>
</table>

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FIGURE CAPTIONS

Figure 1. Approximate ionization energy locations for Mn in ZnS, Ce in SrS, and Cu in SrS. The charge states shown indicate Mn$_{Zn}$ to be a single donor, Ce$_{Sr}$ to be a double donor (with the second donor ionization state corresponding to ionization of the Ce luminescent impurity), and Cu$_{Sr}$ to be a single acceptor. The Ce second donor state corresponds to the luminescent impurity ground state.

Figure 2. The association of Ce$_{Sr}$ and V$_{Sr}$ isolated point defects to form a Ce$_{Sr}$-V$_{Sr}$ defect complex. Expected association-related trends in the defect ionization energies are illustrated; donor and acceptor ionization energies both become more shallow with association due of the coulombic interaction of the charged defect constituents. The charge state of the Ce$_{Sr}$ and V$_{Sr}$ constituents of the defect complex are likely to be +1 and -2, respectively, so that the net charge on the defect complex is expected to be -1. Note that V$_{Sr}$ is a double acceptor.

Figure 3. Possible equilibrium energy band diagrams for a SrS:Cu phosphor layer. (a) corresponds to a simple flat-band situation in which the Fermi level is positioned below midgap due to Cu acceptor doping. This energy band picture implies that a SrS:Cu ACTFEL device should operate via hole injection and transport, since hole injection barriers are much smaller than corresponding electron injection barriers. (b) illustrates a situation in which Fermi-level pinning positions the interface Fermi level in the upper portion of the energy bandgap, as required for electron-injection, and yet allows the bulk Fermi level to be located below midgap, due to Cu acceptor doping.

Figure 4. Photo-induced transferred charge (PIQ) curves demonstrating the superior transport properties of electrons compared to holes in an ACTFEL device with a 1100 nm thick SrS:Cu phosphor layer.

Figure 5. An energy band diagram of an ACTFEL device under bias which illustrates the three mechanisms of space charge generation: field emission, trap-to-band impact ionization, and band-
to-band impact ionization with hole trapping.

Figure 6. An energy band diagram of an ACTFEL device at zero bias which illustrates the two mechanisms of space charge annihilation: electron emission / recombination and hole emission.

Figure 7. Maximum external transferred charge as a function of maximum applied voltage ($Q_{max}$-$V_{max}$) curves obtained at three different frequencies for a SrS:Ce ACTFEL device. The step in $Q_{max}$ above threshold is associated with space charge creation. Above the $Q_{max}$ step the $Q_{max}$-$V_{max}$ slope is approximately equal to the insulator capacitance of the ACTFEL device. Pre-threshold charge transfer is evident and is ascribed to bulk donor ionization, possibly due to the first ionization of Ce$_{Sr}$ donors.

Figure 8. An internal charge - phosphor field ($Q$-$F_P$) curve for a SrS:Ce ACTFEL device obtained at 40 V above threshold. The decrease in charge during the trailing edge portion of the positive applied voltage pulse (and to a lesser extent, the negative pulse) is denoted charge collapse. Charge collapse is attributed to the back injection of conduction band electrons or electrons trapped in shallow states near the anode phosphor / insulator interface.

Figure 9. Temperature-dependent subthreshold voltage-induced transferred charge (VIQ) curves for a SrS:Ce ACTFEL device. These curves provide evidence for the existence of a shallow, i.e., $\sim$0.1 eV donor trap, possibly due to the first ionization energy of a Ce$_{Sr}$-V$_{Sr}$ complex.
Figure 1: Wager et al.
Figure 2: Wager et al.
Figure 3: Wager et al.
Figure 4: Wager et al.
Figure 5: Wager et al.
Figure 6: Wager et al.
Figures 7: Wager et al.
Internal Charge ($\mu$C/cm$^2$) vs. Phosphor Field (MV/cm)

- Charge collapse (+ applied voltage pulse)
- Charge collapse (- applied voltage pulse)

Figure 8: Wager et al.
Figure 9: Wager et al.