Addition of oxygen in the Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce phosphor has been found to nearly double the efficiency and shift the Ce$^{3+}$ 4f-5d emission spectrum to a deeper blue. To understand the effects that oxygen has on the Ce$^{3+}$ 4f-5d emission spectrum, we used a self-consistent-field configuration interaction (SCF/CI) model to calculate the electronic spectrum of oxygen-doped SrS:Ce. By replacing the appropriate number of sulfur ligands with oxygen ligands, the SCF/CI model predicted a blue shift for two different cerium-oxygen bond distances that is in very good agreement with the 730 cm$^{-1}$ blue shift observed for Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce. An analysis of atomic orbital electron populations indicates that changes in covalency of the Ce 5d orbitals upon incorporation of smaller O$^{2-}$ ions causes the observed blue shift. Calculated oscillator strengths indicate that the observed increase in electroluminescent efficiency caused by addition of oxygen is not a result of changes in transition intensities.

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The alternating current thin-film electroluminescent phosphors Sr$_x$Ce and Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce have been found to emit blue light.$^1$ It is of interest to shift the color to a deeper blue and increase the emission efficiency to obtain a blue phosphor suitable for sunlight-readable full color displays. One promising approach is to codope with other ions, since the presence of other impurities in the host lattice can have an impact on both the energy and intensity of the Ce$^{3+}$ emission. For this reason we have studied the effect of the addition of oxygen to the Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce phosphor and find that the efficiency is nearly doubled and the Ce$^{3+}$ emission is shifted to a deeper blue.$^2$

The luminescent and structural properties of Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce were first studied by Peters and Baglio in 1972$^{3,4}$ and have more recently been investigated for electroluminescent display$^{5-7}$ and field emission display phosphors.$^{8,9}$ The Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$ host lattice was found to have a rather complex orthorhombic crystal structure$^3$ containing three slightly different M$^{2+}$ lattice sites (where M is Ca or Sr) with a concentration ratio of roughly 1:2:1. Ce$^{3+}$ ions substitute on M$^{2+}$ lattice sites. Recently, electron paramagnetic resonance (EPR) confirmed three different Ce$^{3+}$ sites in SrGa$_2$S$_4$ with the same 1:2:1 concentration ratio, suggesting that there is no preferential Ce$^{3+}$ in the lattice.$^{10}$ Though the three different M$^{2+}$ sites differ slightly, they are all eightfold coordinated with an antipristmonic symmetry.

The results presented in Ref. 2 are summarized here for convenience. Thin-film Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce samples were rf magnetron sputter deposited from pressed powder targets. The films were doped with oxygen by backfilling with a mixture of argon and oxygen as the sputtering gas. X-ray photoelectron spectroscopy (XPS) confirmed oxygen incorporation. Detailed analysis of the Ce 3d XPS peaks suggested that the added oxygen does interact directly with the Ce$^{3+}$ impurity, with an average of three of the eight Ce-S bonds in the undoped samples replaced with Ce-O bonds in the oxygen-doped samples.$^{2}$ Figure 1a shows electroluminescence emission spectra for both an undoped and an oxygen-doped Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce thin film. A blue spectral shift of 15 nm (733 cm$^{-1}$) was observed when oxygen was introduced into the Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce films. Both spectra show two peaks separated by about 45 nm (2063 cm$^{-1}$). The presence of two peaks is due to spin-orbit coupling, which splits the 4f orbital-derived $^2$F state into $^2$F$_{5/2}$ and $^2$F$_{7/2}$ levels.

To understand the experimental observations, we consider two properties of the host lattice that affect the luminescent center, the lattice symmetry and ion spacing. The former influences both the nature of the splitting pattern and, to a lesser extent, the magnitude of the splitting. In the present case oxygen and sulfur have the same valence state, so it is assumed that oxygen simply substitutes isoelectronically for sulfur, preserving the local symmetry of the luminescent center. The ion spacing affects both the coulombic potential experienced by the valence electrons of the luminescent center and the molecular orbital overlap with neighboring ions. Both effects are generally considered together as the ligand field strength, where it is understood that both increased coulombic interaction and increased covalency (due to increased orbital overlap) increase the field strength.

In the case of the Ce$^{3+}$ 4f $\rightarrow$ 5d emission, the Ce 4f orbitals are compact and shielded from the host lattice by the 5s and 5p electrons and so are insensitive to the ligand field. The 5d orbitals are larger and not shielded, and therefore their energy positions are sensitive to the host lattice. Since levels derived from the 4f orbitals are the lower levels involved in the emission spectroscopy, it is clear that the blue shift of the spectroscopy observed on the addition of oxygen indicates a reduced ligand field affecting the 5d orbitals. This is graphically illustrated in Fig. 2.

According to the spectrochemical series, O$^{2-}$ is considered a stronger-field ligand than S$^{2-}$. The spectrochemical series is based on ligand field splittings measured at the optimum metal-ligand distances found in isolated transition metal complexes, however, and the distance between Ce$^{3+}$ and an O$^{2-}$ ion (r$_{CeO}$) on a S$^{2-}$ site is far

![Figure 1](image-url)
The cluster of quantum ions used to model the undoped SrS:Ce 4f and 5d-derived energy levels consists of thirteen ions. The Ce$^{3+}$ LC was placed at the origin of a Cartesian axis system. Six S$^{2-}$ ions were placed at $\pm a_x/2$ (0.301 nm) and six Sr$^{2+}$ ions were placed at $\pm a_x$ on the $x$, $y$, and $z$ axes. This cluster was embedded in a $15 \times 15 \times 15$ matrix of $+2$ and $-2$ point charges placed at the lattice positions of Sr$^{2+}$ and S$^{2-}$ ions, respectively, to account for the electrostatic contribution of the rest of the host lattice. Point charges on faces, edges, and corners of the cubic array used are given appropriate fractional charges to obtain the proper Madelung potential at the origin.

The XPS measurements indicated an oxygen/sulfur ratio of 3/8 (0.375) in the first coordination sphere. Under the simplified octahedral lattice symmetry, the closest O/S ratio is 2/6 (0.333), so to model the effect of oxygen doping we replace two S$^{2-}$ ions in the above-described cluster with O$^{2-}$ ions. Since some contraction of the Ce-O bond distance is expected, the calculations were performed at two relaxed Ce-O bond distances, 0.285 and 0.275 nm. There are two possible symmetries of the central CeS$_5$O$_7$ cluster, D$_{4h}$ (with the oxygens on the $+z$ and $-z$ axes, for example) and C$_{2v}$ (with oxygens at $+z$ and $+x$, for example). Calculations were performed for both symmetries assuming a Ce-O distance of 0.285 nm. It was found that the total energies of the two clusters were very similar, differing by no more than 0.06 eV, and that the predicted spectroscopy was very similar as well. Thus we present results at the two Ce-O bond distances assuming D$_{4h}$ cluster symmetry.

Results and Discussion

Cerium orbital energy level diagrams for the undoped O$_h$ cluster symmetry and the doped D$_{4h}$ cluster symmetry are shown in Fig. 3. The final levels are indicated using the double-group notation of Bethe, and incorporate both spin-orbit and ligand field effects. In each symmetry the 4f orbitals are split primarily by spin-orbit coupling into $^2T_{2g}$ and $^2E_g$ levels, by some 2000 cm$^{-1}$. These levels are themselves split by small amounts (on the order of 100 cm$^{-1}$) by the ligand field. The 5d orbitals are split primarily by the ligand field into $^2T_{2g}$ and $^2E_g$ states in the case of O$_h$ symmetry and further by smaller spin-orbit interactions. The latter amounts to about 1000 cm$^{-1}$ between $\Gamma_7(^2T_{2g})$ and $\Gamma_8(^2E_g)$. Finally, the energy difference between the ground $\Gamma_7(^2T_{2g})$ level and $\Gamma_8(^2E_g)$ is on the order of 24,000 cm$^{-1}$. Similar energies hold for the cluster with D$_{4h}$ symmetry. Figure 3 also shows the radiative transitions that give rise to the observed emission spectra. Calculated energies and oscillator strengths for these transitions are given for the three clusters in Table I. In the table the transitions are numbered in order of increasing energy according to Fig. 3.

Computational Model

We use an embedded cluster model to treat a luminescent center (LC) in an extended ionic crystal lattice environment. The cluster consists of a small number of ions (including the LC) that are treated quantum-mechanically ("quantum ions") and is embedded in a large array of coulombic point charges constructed to provide the electrostatic effect of the bulk lattice on the quantum ions. Use of this approach with the INDO/S self-consistent-field/configuration interaction (SCF/CI) model has been shown to be effective in predicting the spectroscopy of the Ce$^{3+}$ LC in the host lattices MgS, CaS, SrS, and BaS. A detailed account of the computational approach is given there.

We use the octahedral SrS host lattice rather than the complex orthorhombic crystal structure of Ca$_{0.3}$Sr$_{0.7}$Ga$_2$S$_4$ to model the effect of oxygen doping. This is a reasonable simplification because emission spectra of SrS:Ce and Ca$_{0.3}$Sr$_{0.7}$Ga$_2$S$_4$:Ce are very similar, and we are interested in the change in transition energy caused by addition of oxygen rather than in absolute transition energies.

Figure 2. Energy-level diagram showing how an observed blue shift in Ce$^{3+}$ 4f-5d emission results from decrease in ligand field strength. Energy differences between levels are not to scale and are described in the text.

Figure 3. Energy-level diagrams for Ce$^{3+}$ under (a) octahedral symmetry and (b) D$_{4h}$ symmetry along with the radiative transitions giving rise to the emission spectrum for each.
The experimentally observed Ce$^{4+}$ emission bands are convolutions of the various transitions indicated in Fig. 3 and accompanying vibronic transitions.\textsuperscript{17} As discussed in Ref. 15, transition energies computed using the INDO/S SCF/CI model represent band maxima of absorption processes. Band maxima of the corresponding emission processes are shifted to lower energy, since emission maxima are typically lower in energy than the 0-0 phonon line while absorption maxima are at higher energy than the 0-0 phonon line, see Fig. 4. This so-called Stokes shift (denoted by $\Delta E$ in the figure) can be as large as 0.25-0.50 eV.\textsuperscript{15,18} The phosphors under question are very similar, so $\Delta E$ should be more or less constant. Given that, no explicit account of $\Delta E$ is made since we are interested in relative rather than absolute transition energies.

An approximate vibronic spectrum can be fit from the calculated transition energies and intensities by fitting each transition with a Gaussian curve having a fixed full-width-at-half-maximum (fwhm) and an integrated area equal to the calculated oscillator strength.\textsuperscript{15,19} The purpose of fitting spectra in this way is to provide a visual comparison of the relative intensities and energies of the two features so no attempt is made to properly account for vibrational fine structure. Although a more in-depth analysis could be undertaken, a quantitative comparison of vibrational structure is inappropriate since the calculations assume a different host material (SrS) than that used experimentally (Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$). Figure 1b shows approximate emission spectra generated in this way for SrS:Ce and oxygen-doped SrS:Ce with Ce-O bond distances of 0.285 and 0.275 nm. The asymmetric bimodal distribution observed in the experimental spectra (see Fig. 1a) is clearly reproduced, as is the blue shift caused by addition of oxygen to Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce. $\Delta E$ (Fig. 4) is obvious when comparing the experimental and approximate spectra in Fig. 1 and appears to be on the order of 3000 cm$^{-1}$ (0.37 eV).

Quantitatively the blue shift in the energy of the band maximum of the high-energy component of the 4f-5d emission spectrum is found to be 1470 cm$^{-1}$ for $r_{\text{CeO}} = 0.285$ nm and 960 cm$^{-1}$ for $r_{\text{CeO}} = 0.275$ nm. These results are in good agreement with the experimentally observed blue shift of 733 cm$^{-1}$, given that we have guessed at geometric distortions and have used an octahedral lattice rather than an orthorhombic one. The fact that the predicted blue shift is smaller at $r_{\text{CeO}} = 0.275$ nm suggests that the energy shift is caused by changes in covalency experienced by the Ce 5d orbitals, since there is an opposing crystal field effect when the lattice contracts.

The SCF/CI results provide atomic orbital populations that are a quantitative indication of covalency. The Ce$^{4+}$ ion has the electron configuration [Xe]4f$^2$5d$^0$ in its ground state, so if the interaction of the 5d orbitals and the neighboring S$^2-$ ions was purely ionic, these populations would be zero. Covalent overlap with the filled orbitals of S$^2-$, on the other hand, would cause a small amount of electrons to occupy the 5d orbitals. The total occupation of the cerium 5d orbitals is then a measure of the extent of covalency. Occupations of the Ce 5d orbitals in the Ce$^{3+}$ ground 4f$^3$ state were calculated for the three cases (undoped, doped with $r_{\text{CeO}} = 0.285$ nm, doped with $r_{\text{CeO}} = 0.275$ nm) and are shown in Table II. The trend in populations apparent in Table II shows that the spectroscopic shifts do follow changes in covalency caused by the smaller overlap of the oxygen orbitals with the Ce 5d orbitals.

The efficiency of the Ce$^{4+}$ 4f-5d emission was nearly doubled by addition of oxygen to the Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce phosphor. This is not reflected by the total oscillator strengths predicted for the three model clusters (Table I), indicating that a change in some property other than the intrinsic brightness of the transitions is responsible for the increase in efficiency observed in the electroluminescence. Possibilities include an enhancement of the rate of injection of electrons into the Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$ film caused by changes in the crystal structure, or an increase in the impact cross section of the luminescent center due to presence of oxygen ions in the immediate vicinity of Ce$^{3+}$.

The trend in the total oscillator strengths calculated for the three model clusters is easily understood in terms of the cluster symmetries. Replacement of sulfur ions by oxygen ions relaxes the formal octahedral symmetry of the undoped cluster, causing the increase in

<p>| Table I. Calculated Ce 4f-5d transition energies and oscillator strengths for undoped SrS:Ce and oxygen-doped SrS:Ce with $r_{\text{CeO}}$ of 0.285 and 0.275 nm. |
|---|---|---|---|---|
| Transition | Undoped SrS:Ce | Doped, $r_{\text{CeO}}$ 0.275 nm | $r_{\text{CeO}}$ 0.285 nm |</p>
<table>
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<th>(Fig. 3)</th>
<th>Energy (cm$^{-1}$)</th>
<th>Osc. strengths</th>
<th>Energy</th>
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</tr>
<tr>
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<tr>
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<tr>
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<td>24190</td>
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<td>—</td>
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</tr>
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---

**Figure 4.** Schematic representation of absorption and emission bands displaying Stokes shift between band maxima.
intensity predicted for the doped clusters. When comparing the two doped model clusters, it is apparent that the departure from octahedral symmetry is more pronounced for the longer value of \( r_{CeO} \) since the orbital overlap decreases as \( r_{CeO} \) increases, causing the total oscillator strength to be larger for the model cluster with larger \( r_{CeO} \).

Conclusions

Semiempirical SCF/CI calculations using an embedded cluster model with octahedral symmetry found an increase in 5d-4f transition energies when two sulfur ions were replaced with oxygen ions. Quantitatively, an oxygen-to-anion ratio of 0.333 \((2/6)\) increased the energy of the band maximum of the blue component of the 5d-4f emission spectrum by 1470 cm\(^{-1}\) for a Ce-O bond distance of 0.285 nm and by 960 cm\(^{-1}\) for a Ce-O bond distance of 0.275 nm. The calculated shifts are in good agreement with the experimentally determined shift of \( \sim 730 \) cm\(^{-1}\) that was observed upon addition of oxygen to the \( \text{Ca}_0.5\text{Sr}_0.5\text{Ga}_2\text{S}_4\) :Ce phosphor. An atomic orbital population analysis revealed that the experimentally observed blue shift is due to a decrease in the covalent character of the Ce 5d orbitals upon addition of the smaller O \(^2\) ions on S \(^2\) sites. Computed oscillator strengths indicate that the large increase observed in the efficiency of electroluminescence caused by addition of oxygen is not due to a change in the inherent brightness of the emission.

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