Inorg. Chem. 1993, 32, 639–641 639

Pressure-Induced Luminescence Quenching of Terbium-Doped Oxide Sulfides

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Received August 6, 1992

The photoluminescence of Tb^{3+}- and Eu^{3+}-doped rare earth oxide sulfides has been studied as a function of pressure. The luminescence intensity and lifetime of the $^5D_3$ level of Tb^{3+} is quenched by pressure as a result of the pressure-induced red shift of the interconfigurational $4f^75d$ band, in agreement with the energy gap law of radiationless transitions.

Introduction

Lanthanum oxide sulfides are important host materials for rare earth doped phosphors because the highly efficient f–f luminescence of the dopant can be directly sensitized by the excitation of the broad UV band of the activator.[1-3] These activated phosphors find frequent use in electronic display devices and detectors, as well as remote temperature probes of their surroundings.[4] This work reports on changes in luminescence parameters of Tb^{3+} and Eu^{3+} induced by hydrostatic compression of the crystalline matrix.

The relevant spectroscopic properties of trivalent terbium doped in rare earth oxide sulfides (Ln_2O_2S:Tb, Ln = La, Gd) are most easily reviewed in terms of Figure 1, in which the energy levels of Tb^{3+} are compared with those of Eu^{3+}.[5-7] These two activator ions show narrow, weak bands characteristic of f–f transitions and broad, intense bands involving different orbitals, both well below the conduction band of the host crystal.[8-10] Excitation spectra place the absorption edge of La_2O_2S:Tb about 2000 cm^{-1} above the $^5D_3$ state at 26 500 cm^{-1}. The broad bands are rare earth activators arise from allowed transitions either to interconfigurational (IC) or charge-transfer (CT) states.[1,3,11,12] The extra stability of the half-filled 4f shell determines that the lowest broad absorption band arises from transitions to the IC state ($4f^8 \rightarrow 4f^75d$) in the case of Tb^{3+} and to the CT state ($4f^6 \rightarrow 4f^73p^{-1}$) in Eu^{3+}-doped oxide sulfides.

UV excitation into the IC and CT states directly feeds discrete 4f states and gives the visible $^5D_i \rightarrow {}^7F_j$ luminescence characteristic of these rare earth ions, where i = 4, 3 for Tb^{3+} and i = 0, 1, 2 for Eu^{3+} in these Ln_2O_2S matrices at room temperature. Low activator concentrations are necessary to avoid the dominance of luminescence quenching by cross relaxation over the radiative and nonradiative processes characteristic of single optical centers. The Tb^{3+} luminescence in La_2O_2S or Gd_2O_2S powders is especially susceptible to concentration quenching, and $^5D_3$ emission is only observed from highly dilute samples.[13,14]

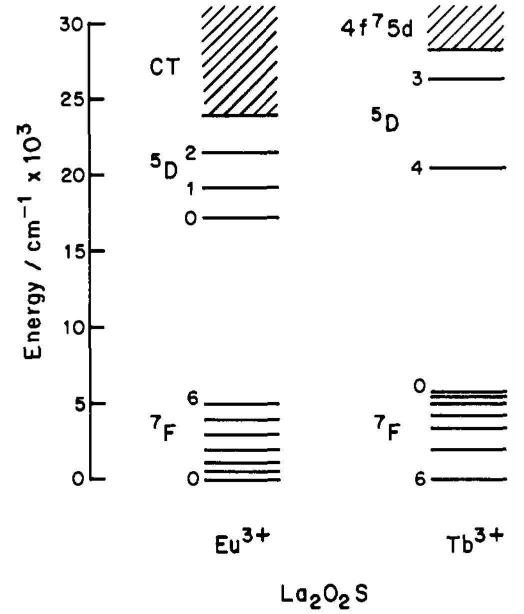

Figure 1. Energy level diagram for Tb^{3+} and Eu^{3+} ions in La_2O_2S.

Thermal quenching of the f–f luminescence is observed because the excitation bands can be repopulated by the long-lived ^5D_i states with probability depending exponentially on the energy gap.[6,7,15-17] Thus, the observed activation energies for sequential, T-induced luminescence quenching are consistent with the known energies of the ^5D_i states. The Boltzmann factor responsible for nonradiative deactivation can be altered by temperature through changes in population ratios or by pressure-induced changes of the energy gap between the coupled states. This report concerns

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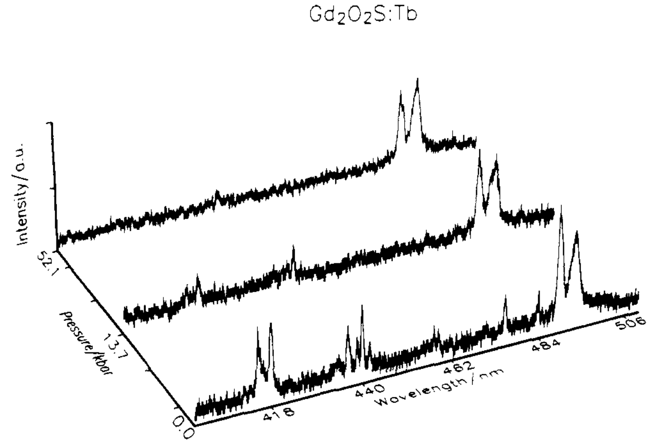

Figure 2. Luminescence spectra of Gd_2O_2S:Tb at 1 atm, 14 kbar, and 52 kbar. Intensities are normalized at 493 nm ($^5D_4 \rightarrow {}^7F_6$).

P-induced quenching of Tb^{3+} luminescence, which is compared to results for Eu^{3+} reported previously by Webster and Drickamer.[18]

Experimental Section

The Tb^{3+} phosphor powders obtained from USR Optonix analyzed 0.12 mol % in La_2O_2S:Tb and 0.034 mol % in Gd_2O_2S:Tb. Phosphor samples from Sylvania had a dopant level of 0.44 mol % in La_2O_2S:Eu. The activator ions are statistically distributed over the Ln^{3+} host sublattice in these isomorphic materials with C_{3v} site symmetry.[19]

The pressure experiments in the 0–50-kbar range are carried out in diamond anvil cells of Merrill–Bassett design.[20] The 1-mm thick 316 stainless steel gasket with a 0.25-mm sample hole is sandwiched between the 0.6-mm diameter diamond anvils. The sample powder and ruby chips are suspended in a 4:1 methanol–ethanol fluid to provide hydrostatic pressure within the metal gasket hole. The pressure is measured to ±2 kbar with the ruby luminescence scale[21] by observing the Cr^{3+} R_1 line shift excited with a 40-mW Ar^+ laser.

The phosphors are excited at 325 nm with an Omnichrome 56 10-mW He/Cd laser or at 337 nm with a Laser Energy 60-μJ pulsed N_2 laser. A 150-W xenon lamp is used to record uncorrected luminescence excitation spectra. Luminescence signals are stored in a LeCroy 9400 oscilloscope, sent to a PC386 computer and analyzed/plotted with the AXUM 1.2 program. Pressure changes of Tb^{3+} and Eu^{3+} luminescence are studied by measuring the pressure effects on the transition energies, intensities, and lifetimes of f–f luminescence and the pressure shift of the UV excitation spectra.

Results

Pressure-induced quenching of Tb^{3+} luminescence intensities (I) is illustrated in Figure 2. The blue $^5D_3 \rightarrow {}^7F_j$ emission around 418 and 450 nm strongly diminishes with increasing pressure relative to the green $^5D_4 \rightarrow {}^7F_j$ spectrum located beyond 480 nm. The pressure effects are essentially identical for the Gd and La host crystals, although small and subtle spectra changes within the $4f^8$ multiplets of Tb^{3+} were not analyzed. In agreement with earlier observations,[18] the Eu^{3+} phosphor exhibits an intensity enhancement of the blue $^5D_2 \rightarrow {}^7F_j$ emission at higher pressure (Figure 3). The temporal behavior of I can be described by one lifetime τ, since deviations from linear ln I vs t plots are insignificant in our experiments. The pressure dependence of τ mirrors the pressure-induced changes in intensities for Tb^{3+} and Eu^{3+} activators,[18,22] as shown in Figures 4 and 5. The data are insufficiently precise to substantiate the qualitative result that the ratio I/τ is independent of pressure.

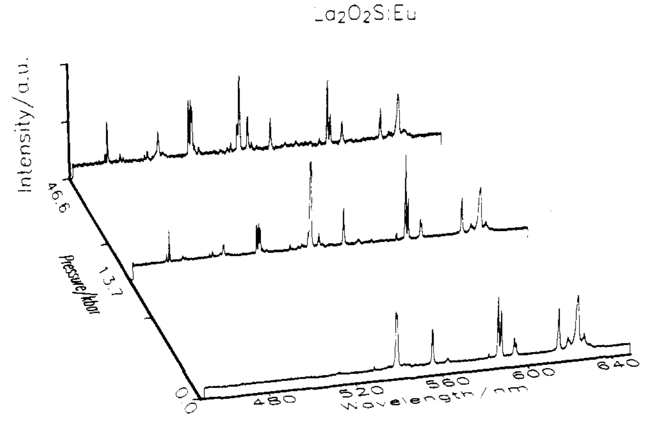

Figure 3. Luminescence spectra of La_2O_2S:Eu at 1 atm, 14 kbar, and 47 kbar. Intensities are normalized at 625 nm ($^5D_0 \rightarrow {}^7F_2$).

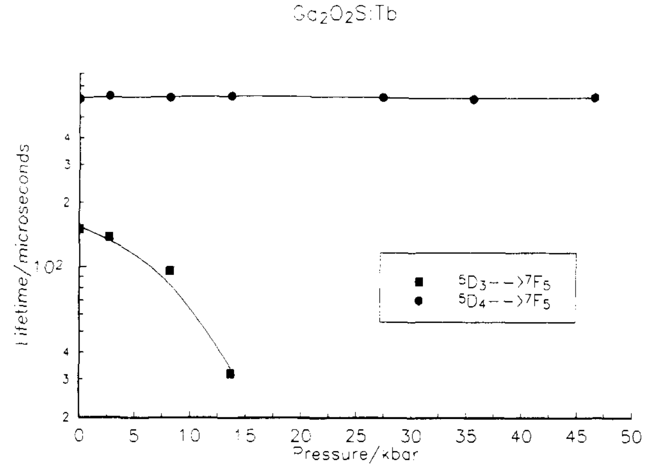

Figure 4. Luminescence lifetimes of the $^5D_4$ and $^5D_3$ states of Gd_2O_2S:Tb as a function of pressure.

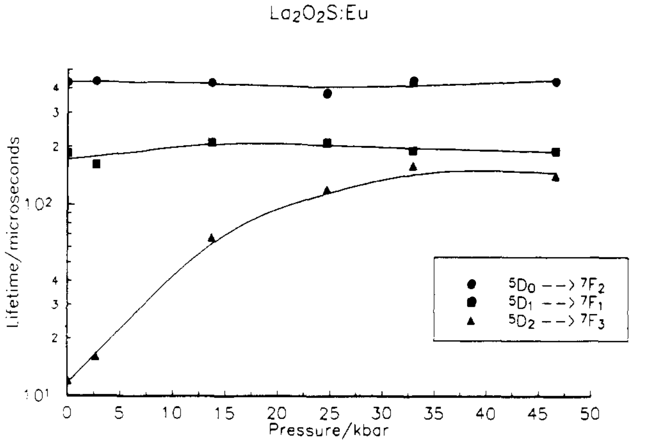

Figure 5. Luminescence lifetimes of the $^5D_0$, $^5D_1$, and $^5D_2$ states of La_2O_2S:Eu as a function of pressure.

The large and opposite pressure effects on I and τ of these two activators could be caused by appropriate modifications of the energy level spacings of the two systems. The f–f transitions demonstrate only small, monotonic red shifts of ≈–0.3 cm^{-1}/kbar for the $^5D_4$ luminescence of Tb^{3+} and as much as ≈–0.5 cm^{-1}/kbar for the $^5D_2$ luminescence of Eu^{3+} in the 0–50-kbar range. As expected for forbidden, narrow-band emitters, the 4f levels are well screened by the Xe core electrons and compression of the surroundings has only a small effect on these energy levels.[23-25]

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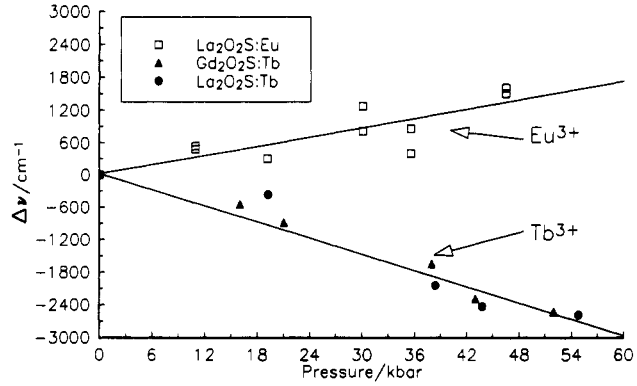

Figure 6. Pressure dependence of the excitation band edge for Tb^{3+} in Gd_2O_2S and La_2O_2S, monitored at 544 nm, and for Eu^{3+} in La_2O_2S, monitored at 538 and 625 nm.

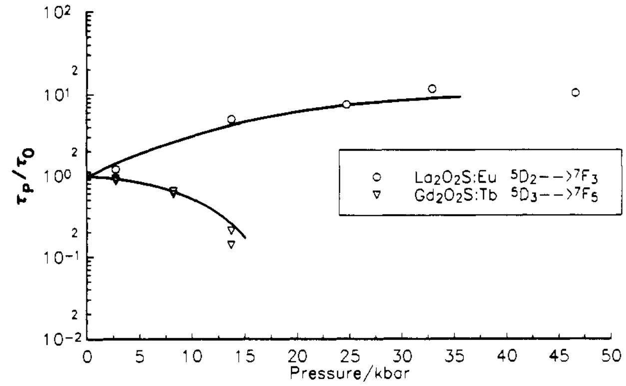

Figure 7. The lifetime ratio τ_P/τ_0 observed for the Tb^{3+} $^5D_3$ and Eu^{3+} $^5D_2$ luminescence and calculated according to eq 1 (—).

These shifts are too small to explain the observed large $I(P)$ and $\tau(P)$ behavior.

On the other hand, the allowed UV excitation bands of these two ions show large pressure shifts, as illustrated in Figure 6. The excitation spectra taken in the 300–400-nm spectral region show a pressure-induced red shift of -46 cm^{-1}/kbar for Tb^{3+} as opposed to a $+32$ cm^{-1}/kbar blue shift for Eu^{3+}. The greater magnitude of $d\nu/dP$ for Tb^{3+} relative to Eu^{3+} is correlated with the observed $d\tau/dP$, since the $^5D_3$ lifetime of Tb^{3+} decreases nearly twice as fast as the $^5D_2$ lifetime of Eu^{3+} increases. Thus the pressure quenching of the Tb^{3+} luminescence is readily associated with the decrease in the $^5D_3$–IC energy gap, and the enhanced blue luminescence of Eu^{3+} is attributed to the widening of the $^5D_2$–CT energy separation. It is noted that large pressure-induced red shifts have also been observed in other interband excitations, e.g., the $4f^75d$ state of divalent Eu^{2+} in CaF_2[26] and the $nd(n + 1)p$ state of transition metal glyoximes.[27]

Discussion

The luminescence properties of rare earth phosphors are typically discussed in terms of the single configurational coordinate model, which Struck and Fonger applied successfully to explain thermal quenching.[1,6,7,15,16] In these compounds the relevant coordinate Q is the Ln^{3+}–S^{2-} distance. Large Franck–Condon offsets ΔQ between the parabolic energy minima of the UV interconfigurational (IC) or charge-transfer (CT) state and the various $4f^n$ energy surfaces assure strong coupling between them, so the model of an activated process for nonradiative transition probabilities can be applied. Since oxide sulfides are relatively soft materials, the large parabola offsets are readily perturbed by pressure. Also, a single activation energy ΔE can be used to describe the deactivation rate for large ΔQ, irrespective of the orbital character of the quenching state. In the strong-coupling case of this simple configurational model, the energy gap is related to the observed lifetime by $\tau^{-1} = k_r + k_{nr}^0 e^{-\Delta E/k_bT}$, where k_r is the radiative rate constant and k_{nr}^0 reflects the temperature-independent factor in the nonradiative process. The lifetime ratio at pressure P relative to 1 atm (τ_0) is then given by

$$\tau_P/\tau_0 = \frac{a + e^{-\Delta E_0/k_bT}}{a + e^{-\Delta E_P/k_bT}} \qquad (1)$$

where $k_bT = 208$ cm^{-1} and $a = k_r/k_{nr}^0$ is assumed to be pressure-independent. The adjustable parameter a is optimized with the pressure shift data and equals 5.7×10^{-4} for Tb^{3+} and 1.3×10^{-7} for Eu^{3+}. Errors in a are large for our limited data set, which explains in part the factor of 40 difference in the $a(Eu^{3+})$ value computed by Webster and Drickamer[18] from their intensity data over a larger pressure span. Figure 7 shows a general agreement between the observed and calculated τ ratios of the $^5D_3$ (Tb^{3+}) and $^5D_2$ (Eu^{3+}) states as a function of pressure. In agreement with this model, the other ^5D_i states with activation energies far exceeding 208 cm^{-1} do not show pressure sensitivities in τ at room temperature.

The opposite direction of the pressure-induced shifts of the IC and LMCT states can be understood by examining the observed trends in ν_{IC} and ν_{CT} of lanthanide compounds as a function of the number of f electrons in the ground state.[28-31] The band peak positions of the IC states correlate with the nephelauxetic parameter β ($\Delta\nu_{IC} \propto \Delta\beta$), and the CT states correlate with the electronegativity χ_L of the ligand anion ($\Delta\nu_{CT} \propto \Delta\chi_L$). Since χ_L changes in opposite order as the nephelauxetic series (which is a measure of the tendency to covalent bonding),[30] an increase in pressure can lead to opposing spectral shifts for the two types of transitions. Earlier studies confirm the general expectation that the crystal field strength increases and the Racah B parameter decreases upon compression.[32,33] Pressure increases covalency by orbital mixing and reduces interelectronic repulsion, thus lowering the IC state of terbium in lanthanum oxide sulfides. Similarly, pressure increases the electronegativity of the polarizable sulfur anion; thus, more energy is required to transfer an electron to the central metal ion and a blue shift of the CT band results for europium in Ln_2O_2S.

In conclusion, the pressure shift of energy levels in these soft ceramic phosphors is at least 1 order of magnitude smaller for forbidden $4f^n$ intrashell transitions compared to the allowed bands resulting from interconfigurational or charge-transfer transitions. If the energy gap separating the broad excitation band from the narrow luminescent band is not large compared to k_bT, then pressure-induced level shifts are responsible for large changes in the nonradiative transition rates of the emitting state. Hence certain $^5D_i \rightarrow {}^7F_j$ decay channels of these efficient luminescent materials can be very sensitive to P or T changes, and I or τ measurements can be used to monitor pressure or temperature changes in the phosphor's surroundings.

Acknowledgment. This research was supported in part by funds provided EG&G Energy Measurements from the Department of Energy and the Electric Power Research Institute and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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