

# Effect of pressure on luminescence properties of $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$

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We report the effect of pressure on  $d \rightarrow f$  luminescence properties of  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  up to  $\sim 300$  kbar. We observed that the  $d \rightarrow f$  luminescence upon compression exhibited a large redshift in energy and a strong quenching in intensity. The pressure-induced redshift was explained by an increased crystal-field strength and nephelauxetic effect. We attributed the pressure-induced quenching in the intensity to a pressure-induced crossing of the conduction band edge of  $\text{Lu}_2\text{S}_3$  and the emitting  $5d$  state of  $\text{Ce}^{3+}$  on the basis of temperature-dependent luminescence intensity measurements. A quantitative analysis of the temperature dependence at several pressures was completed and analyzed using a photoionization model. Excellent agreement of the model with the experimental results was found.

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## I. INTRODUCTION

Recently increased attention has been paid to parity-allowed  $4f^{n-1}5d \rightarrow 4f^n$  luminescence transitions (informally referred to as  $d \rightarrow f$  transitions) of divalent and trivalent lanthanides. The recent work has been motivated by a phenomenological desire to further understanding  $d \rightarrow f$  luminescence processes<sup>1</sup> and by a technological desire to develop improved tunable solid-state laser, scintillator, and phosphor materials in the vacuum ultraviolet (VUV), ultraviolet (UV),<sup>2</sup> and blue.<sup>3</sup>

Since the efficiency of the  $d \rightarrow f$  luminescence transition of  $\text{Ce}^{3+}$  varies widely with host material [e.g.,  $\sim 75\%$  in  $\text{Ce}^{3+}:\text{Lu}_2\text{SiO}_5$  (Ref. 4) 0% in  $\text{Ce}^{3+}:\text{Lu}_2\text{O}_3$  (Ref. 5)], great effort has been devoted to understanding the mechanisms that control the  $d \rightarrow f$  luminescence transition in  $\text{Ce}^{3+}$  systems. Several mechanisms of  $5d \rightarrow 4f$  luminescence quenching in  $\text{Ce}^{3+}$ -activated systems have been proposed in the literature,<sup>6,7</sup> but a definitive understanding of the factors responsible for controlling the efficiency of  $\text{Ce}^{3+}$  has proved elusive. A  $5d$ -electron photoionization mechanism proposed by Yen<sup>7</sup> is currently the most commonly accepted model.

Based on the photoionization mechanism, three processes are possible for electrons in the lowest energy of the  $5d$  state [ $5d(1)$ ] of  $\text{Ce}^{3+}$  (Fig. 1). When the emitting  $5d(1)$  state of  $\text{Ce}^{3+}$  is well below the conduction band [Fig. 1(a)], highly efficient  $\text{Ce}^{3+}$  emission is expected to occur because electrons are not delocalized from the emitting  $5d(1)$  state to the conduction band through thermal ionization ( $\Delta E \gg kT$ ). When the emitting  $5d(1)$  state is below, but thermally accessible to the conduction band [Fig. 1(b)], temperature-dependent  $\text{Ce}^{3+}$  emission intensity is expected ( $\Delta E \sim kT$ ). When the emitting  $5d(1)$  state is resonant with the conduction band [Fig. 1(c)], quenching is expected because electrons are efficiently delocalized from the emitting  $5d(1)$  state to the conduction band and decay nonradiatively through host lattice processes.

The primary effect of pressure is to shorten bond lengths in materials. This leads to an increase in crystal-field strength and covalency. Band gaps ( $E_g$ ) of host materials can increase or decrease with pressure, depending on the details of

the band structure. With pressure, we can systematically vary the energy of the emitting  $5d(1)$  state through a pressure-induced increase in the crystal-field splitting and decrease in the barycenter position of the  $5d$  configuration of  $\text{Ce}^{3+}$ . As a result, we have the unique ability with pressure to control the activation energy between the emitting  $5d(1)$  state of  $\text{Ce}^{3+}$  and the host lattice conduction band edge and new opportunities to understand the  $d \rightarrow f$  luminescence process of  $\text{Ce}^{3+}$ .

Numerous existing  $\text{Ce}^{3+}$ -activated materials exhibit  $d \rightarrow f$  luminescence in the VUV and the far-UV (Ref. 8) and are not suitable for high-pressure luminescence studies because of the absorption cutoff edge of the diamond windows used in our experiment to generate pressure.  $\text{Ce}^{3+}$  luminescence ranging from the near-UV to the visible occurs in several  $\text{Ce}^{3+}$ -activated systems. Some of these systems such as  $\text{Lu}_2\text{SiO}_5$  ( $L = \text{Lu}, \text{Y}, \text{Gd}, \text{and Yb}$ ) (Ref. 4) exhibit  $\text{Ce}^{3+}$  multsites that hinder the understanding of the  $d \rightarrow f$  luminescence transition of  $\text{Ce}^{3+}$  because of overlapping spectral features and energy transfer between sites. In this work, we use  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  to investigate the effect of pressure on the  $d \rightarrow f$  luminescence transition of  $\text{Ce}^{3+}$ .  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  is a desirable system because of containing only one crystallographical site for  $\text{Ce}^{3+}$  in Ref. 9 and because the pressure dependence of its crystal structure and host lattice electronic

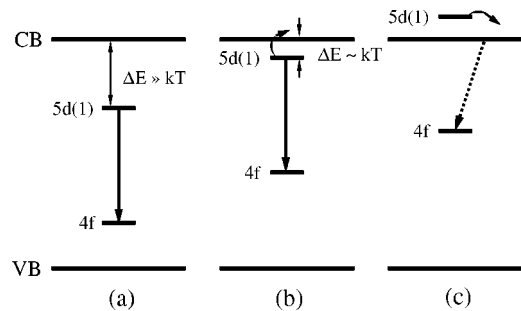


FIG. 1. Energy level diagram governing the  $d \rightarrow f$  luminescence transition of  $\text{Ce}^{3+}$ . CB and VB represent the conduction and valence bands of the host lattice, respectively.  $5d(1)$  and  $4f$  represent the emitting state and the ground state ( ${}^2F_{5/2}$ ) of  $\text{Ce}^{3+}$ , respectively.  $\Delta E$  is the activation energy between the emitting  $5d(1)$  state of  $\text{Ce}^{3+}$  and the conduction band edge of the host lattice.

band structure are known.<sup>10</sup> Consequently,  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  provides an excellent opportunity for obtaining a more complete description of the physical processes that control the luminescence of  $\text{Ce}^{3+}$ .

$\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  exhibits efficient  $d \rightarrow f$  emission in the red at ambient conditions and is expected to be a useful scintillator in the red range.<sup>11</sup>  $\text{Lu}_2\text{S}_3$  possesses a corundum structure (space group  $R\bar{3}c$ ) with the six-S-coordinated Lu site being trigonal antiprismatic (point symmetry  $C_{3v}$ ).<sup>9</sup> Grzechnik<sup>10</sup> observed that  $\text{Lu}_2\text{S}_3$  undergoes a reversible structural transformation from the corundum structure ( $R\bar{3}c$ ) to the  $\text{Th}_3\text{P}_4$ -type structure ( $I\bar{4}3d$ ) at  $\sim 50$  kbar and that the band structure changes from a direct band gap ( $E_g = \sim 3.2$  eV at ambient pressure) to an indirect band gap (estimated  $E_g = 2.0\text{--}2.5$  eV at  $\sim 100$  kbar) as a result of the pressure-induced structural transformation. The large pressure effects observed for this host material provide a unique opportunity for us to use pressure to systematically vary the activation energy ( $\Delta E$ ) between the emitting  $5d(1)$  state of  $\text{Ce}^{3+}$  and the conduction band edge of the host lattice. We can therefore expect strong effects of pressure on the luminescence properties of  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$ .

## II. EXPERIMENT

High-pressure luminescence was performed on a 1-m Spex 1702/04 spectrometer equipped with a standard photon-count detecting system. An argon-ion laser was used to excite  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$ . A  $\sim 100$ -mW output power of 457.9, 488.0, or 514.5 nm was used. For experiments above 120 kbar, a dye laser pumped with the argon-ion laser was used as an additional excitation source ranging over 570–620 nm. All luminescence spectra were corrected for the spectral response of the measurement instrument.

Pressure was generated with a modified Merrill-Basset diamond anvil cell (DAC) capable of reaching  $\sim 300$  kbar. As the pressure transmitting medium, a transparent spectroscopic oil (1 cst viscosity polydimethylsiloxane) was used.  $\text{Lu}_2\text{S}_3$  was soluble in the more commonly used alcohol pressure medium (a mixture of 4:1 methanol:ethanol). The spectroscopic oil remained hydrostatic at room temperature up to  $\sim 200$  kbar. For high-pressure luminescence experiments below room temperature, a closed-cycle refrigerator was used to cool the DAC loaded with the sample. The standard ruby  $R$ -line luminescence technique was used for pressure determination.

The  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  single-crystal samples used in this study were grown using a chemical vapor transport method<sup>12</sup> and were kindly provided by the Institute for Laser Physics of the University of Hamburg.

## III. PRESSURE-INDUCED REDSHIFT

Representative 295-K luminescence spectra of  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  at several pressures are shown in Fig. 2. We observed two overlapping luminescence bands ( $\sim 596.0$  and  $\sim 677.5$  nm at ambient pressure), which originate from transitions between the lowest-energy state [ $5d(1)$ ] of the  $5d$

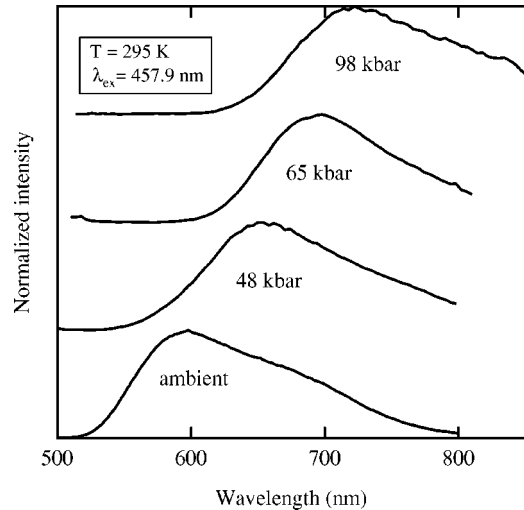


FIG. 2. Representative 295-K luminescence spectra of  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  at several pressures upon excitation at 457.9 nm. The spectra are normalized to peak intensity.

excited configuration and the two spin-orbit split states ( $^2F_{5/2}$  and  $^2F_{7/2}$ ) of the  $4f$  ground configuration of  $\text{Ce}^{3+}$ . The two bands exhibited a strong redshift [ $-30(3)$   $\text{cm}^{-1}/\text{kbar}$ ] with pressure up to  $\sim 100$  kbar.

Parity-allowed  $5d \rightarrow 4f$  emission occurs in many  $\text{Ce}^{3+}$  systems because of the absence of high-energy  $4f$  states. The  $5d \rightarrow 4f$  transition usually exhibits intense, broad luminescence bands at energies ranging from the ultraviolet to the near infrared, depending on the host lattice.<sup>8</sup> In general, the greater spatial extent of the  $5d$  orbital relative to the  $4f$  orbital is responsible for broad luminescence and absorption bands due to the strong coupling of the  $5d$  electron with the lattice. Large effects of pressure on  $d \leftrightarrow f$  transitions are expected because of the strong coupling of the  $5d$  electron with the lattice.

The emitting  $5d(1)$  state of  $\text{Ce}^{3+}$  is the lowest-energy state of the crystal-field split  $5d$  configuration. Its shift direction and magnitude with pressure depend in principle on the variation of both the  $5d$  barycenter energy and the crystal-field strength with pressure. An increase in crystal-field strength is expected with pressure because of bond compression. As a result, an increase in the overall crystal-field splitting of the  $5d$  configuration is expected with pressure. According to the nephelauxetic effect, the  $5d$  barycenter energy is controlled by covalency. The pressure-induced increase in covalency resulting from bond compression is expected to lead to a reduction in the  $5d$  barycenter energy. We therefore expect that pressure induces increases in both the crystal-field strength and the covalency will lead to a redshift for the  $5d(1) \rightarrow 4f$  emission.

Our previous high-pressure luminescence studies for several  $\text{Ce}^{3+}$  systems<sup>13</sup> demonstrated redshifts for  $\text{Ce}^{3+}$  in  $\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$  [ $-13(1)$   $\text{cm}^{-1}/\text{kbar}$ ] and  $\text{Lu}_2\text{SiO}_5$  [ $-19(3)$   $\text{cm}^{-1}/\text{kbar}$ ]. Kitamura *et al.*<sup>14</sup> also observed a redshift for the  $\text{Ce}^{3+}$  emission in  $\text{Ce}^{3+}$ -doped fluoroaluminate glass [ $-16(3)$   $\text{cm}^{-1}/\text{kbar}$ ]. The larger redshift [ $-30(3)$   $\text{cm}^{-1}/\text{kbar}$ ] in  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  relative to the other reported  $\text{Ce}^{3+}$  systems is due to the more compressible nature of the sulfide lattice. A

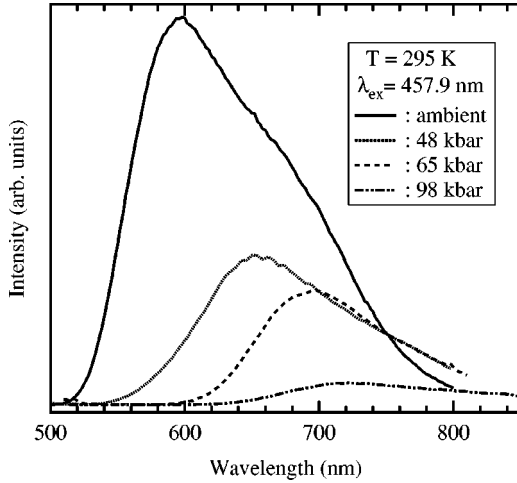


FIG. 3. Representative 295-K luminescence spectra of  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  at several pressures upon excitation at 457.9 nm.

pressure-induced redshift is also expected to occur for  $4f^{n-1}5d \rightarrow 4f^n$  emission of other lanthanide ions. Tyner and Drickamer, for example, observed redshifts (from  $-7$  to  $-37 \text{ cm}^{-1}/\text{kbar}$ ) of the  $4f^65d \rightarrow 4f^7$  emission in some  $\text{Eu}^{2+}$ -doped oxides ( $\text{CaAl}_2\text{O}_4$ ,  $\text{SrAl}_2\text{O}_4$ ,  $\text{Ba}_2\text{SiO}_4$ ,  $\text{Ca}_2\text{P}_2\text{O}_7$ ,  $\text{CaBPO}_5$ , and  $\text{SrBPO}_5$ ).<sup>15</sup> Yoo *et al.*<sup>16</sup> observed a redshift of  $-15 \text{ cm}^{-1}/\text{kbar}$  for the  $4f^55d \rightarrow 4f^6$  emission of  $\text{Sm}^{2+}$  in  $\text{SrF}_2$ .

#### IV. PRESSURE-INDUCED QUENCHING

In addition to the pressure-induced redshift of the  $5d(1) \rightarrow 4f$  emission, a rapid decrease in the  $\text{Ce}^{3+}$  luminescence intensity was observed upon compression at 295 K (Fig. 3). At 98 kbar, the intensity was a factor of  $\sim 20$  weaker than at ambient pressure. With increasing pressure above 98 kbar, the intensity continued to decrease until a complete quenching occurred at  $\sim 120$  kbar.

Above  $\sim 120$  kbar, two additional luminescence experiments were designed in an attempt to understand the origin of the pressure-induced quenching. First, we wanted to see if the quenching was due to shifting of the  $4f \rightarrow 5d(1)$  absorption band of  $\text{Ce}^{3+}$  away from our initial excitation wavelength ( $\lambda_{\text{ex}} = 457.9 \text{ nm}$ ). Consequently, we considered several excitation wavelengths expected to match the absorption band based on estimated positions of the absorption band using the known pressure shift of the emission. Neither argon laser excitation at 488 and 514 nm nor dye laser excitation over the range 575–620 nm was able to produce luminescence between  $\sim 120$  and  $\sim 300$  kbar. Second, we completed 20-K luminescence experiments. No  $\text{Ce}^{3+}$  emission at 20 K was observed between  $\sim 120$  and  $\sim 300$  kbar with any of the excitation wavelengths used in the study.

Upon decompression, the  $\text{Ce}^{3+}$  luminescence reappeared below  $\sim 100$  kbar. At  $\sim 90$  kbar,  $\sim 48$  kbar, and ambient pressure, we completed three series of luminescence experiments between 20 and 295 K during decompression. We observed a strong thermal quenching of  $\text{Ce}^{3+}$  luminescence at  $\sim 90$  kbar (top in Fig. 4) and a weak thermal quenching at  $\sim 48$  kbar (middle in Fig. 4). At ambient pressure, we observed no ther-

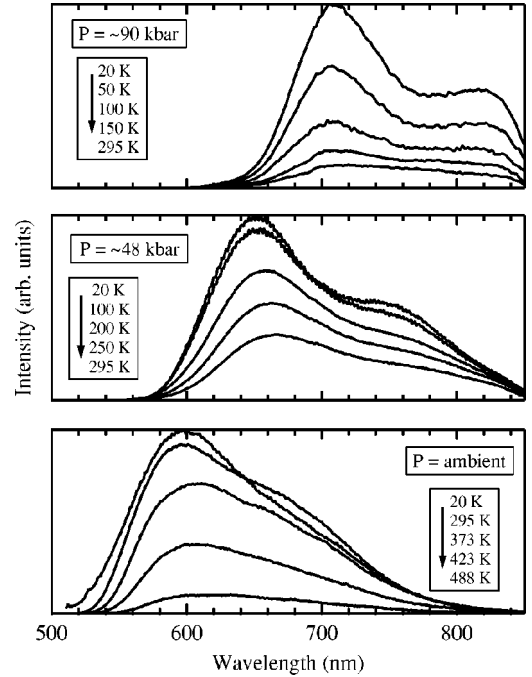


FIG. 4. Representative luminescence spectra of  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  at several temperatures upon excitation at 457.9 nm. Top for  $\sim 90$  kbar, middle for  $\sim 48$  kbar, and bottom for ambient pressure.

mal quenching of the  $\text{Ce}^{3+}$  luminescence intensity between 20 and 295 K (bottom in Fig. 4). We also completed a variable-temperature luminescence experiment on a bulk  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  sample at ambient pressure above room temperature and found that the  $\text{Ce}^{3+}$  luminescence began quenching at  $\sim 320$  K and decreased by a factor of  $\sim 10$  at 488 K (bottom in Fig. 4). The intensity of the  $\text{Ce}^{3+}$  luminescence at  $\sim 90$  kbar,  $\sim 48$  kbar, and ambient pressure as a function of temperature is presented in Fig. 5.

Upon compression, we also observed a gradual change in the appearance of the sample from transparent at ambient pressure to orange-brown at high pressure. Grzechnik<sup>10</sup> used high-pressure x-ray diffraction, Raman spectroscopy, and optical reflectivity on  $\text{Lu}_2\text{S}_3$  to observe a reversible structural transformation from the corundum structure ( $R\bar{3}c$ ) to the  $\text{Th}_3\text{P}_4$ -type structure ( $I\bar{4}3d$ ) at  $\sim 50$  kbar and also to observe a change in the energy band structure from a direct band gap ( $E_g = \sim 3.2 \text{ eV}$  at ambient pressure) to an indirect band gap ( $E_g = 2.0\text{--}2.5 \text{ eV}$  at  $\sim 100$  kbar) during the pressure-induced structural transformation. With increasing pressure, Grzechnik<sup>10</sup> further observed a weak blueshift of the energy band gap from ambient pressure to the phase transition pressure and a strong redshift after the structural transformation. These facts allow us to conclude that the conduction band edge of  $\text{Th}_3\text{P}_4$ -type  $\text{Lu}_2\text{S}_3$  ( $-100$  to  $-200 \text{ cm}^{-1}/\text{kbar}$ ) shifts red at a faster rate than the emitting  $5d(1)$  state of  $\text{Ce}^{3+}$  ( $\sim -30 \text{ cm}^{-1}/\text{kbar}$ ).

We therefore attribute the pressure-induced luminescence quenching to a pressure-induced crossing of the conduction band edge of  $\text{Lu}_2\text{S}_3$  and the emitting  $5d(1)$  state of  $\text{Ce}^{3+}$ . We can develop an interpretation based on the photoionization mechanism to explain the quenching behavior. In the

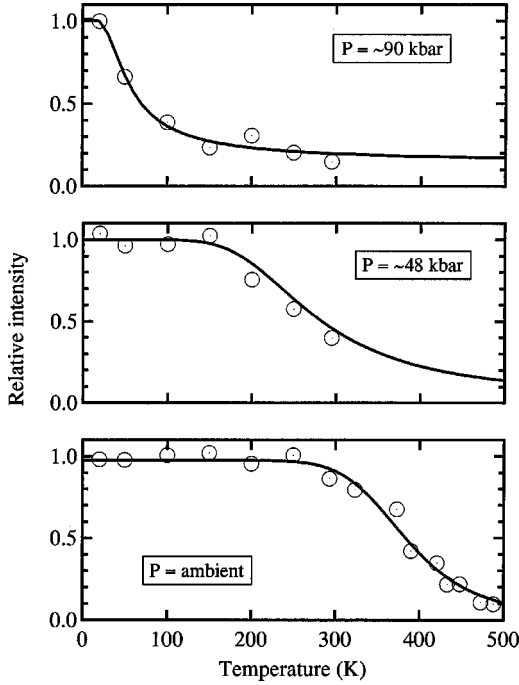


FIG. 5. Variation of relative intensity of  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  at  $\sim 90$  kbar (top),  $\sim 48$  kbar (middle), and ambient pressure (bottom) with temperature. The open circles represent the experimental data and the solid lines represent the calculated results using Eq. (1) and the values for  $\alpha$  and  $\Delta E$  in Table I.

photoionization mechanism, the location of the emitting  $5d(1)$  state relative to the host conduction band edge is the controlling factor in governing the  $\text{Ce}^{3+}$  luminescence intensity. The pressure behavior of the luminescence intensity in the low-pressure regime (before the structural transformation), intermediate-pressure regime (between  $\sim 50$  and  $\sim 120$  kbar), and high-pressure regime (above  $\sim 120$  kbar) is readily attributable to the three processes (a), (b), and (c), respectively, of Fig. 1.

Upon compression, we decrease the activation energy ( $\Delta E$ ) between the emitting  $5d(1)$  state and the conduction band edge and ultimately stabilize the quenched, resonant  $5d(1)$  state of  $\text{Ce}^{3+}$  in  $\text{Lu}_2\text{S}_3$ . When a  $5d$  electron of  $\text{Ce}^{3+}$  is delocalized from the emitting  $5d(1)$  state to the conduction band, it is commonly accepted that the delocalized electron nonradiatively relaxes back to the ground  $4f$  state of  $\text{Ce}^{3+}$  and, as a consequence, no  $\text{Ce}^{3+}$  luminescence occurs.<sup>7,17</sup>

The experimental data for the temperature dependence of the  $\text{Ce}^{3+}$  luminescence intensity ( $I$ ) in Fig. 5 can be simply analyzed in a simple way through

$$I(T) = \frac{I_0}{1 + \alpha \exp(-\Delta E/kT)}, \quad (1)$$

where  $\Delta E$  corresponds to the activation energy between the emitting  $5d(1)$  state of  $\text{Ce}^{3+}$  and the conduction band edge of  $\text{Lu}_2\text{S}_3$  and  $\alpha$  is a frequency factor whose physical meaning is discussed below. A fit of Eq. (1) to the data of Fig. 5 led to

TABLE I. Values for the parameters  $\alpha$  and  $\Delta E$  ( $\text{cm}^{-1}$ ) appearing in Eq. (1) for  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$  at ambient pressure,  $\sim 48$  kbar, and  $\sim 90$  kbar. Standard deviations for the parameters  $\alpha$  and  $\Delta E$  are given in parentheses.

| $P$                             | Ambient              | $\sim 48$ kbar     | $\sim 90$ kbar     |
|---------------------------------|----------------------|--------------------|--------------------|
| $\alpha$                        | $1.0(3) \times 10^4$ | $7(2) \times 10^1$ | $6(1) \times 10^0$ |
| $\Delta E$ ( $\text{cm}^{-1}$ ) | 2477(280)            | 836(150)           | 88(14)             |

excellent agreement with the experiments at ambient pressure,  $\sim 48$  kbar, and  $\sim 90$  kbar using the values for  $\alpha$  and  $\Delta E$  presented in Table I.

From Table I, we see that both the activation energy ( $\Delta E$ ) and the frequency factor ( $\alpha$ ) strongly decrease with increasing pressure. The strong decrease in the activation energy with pressure is expected. A rough estimation for the redshift of the conduction band of the high-pressure phase  $\text{Lu}_2\text{S}_3$  was made from our data in Table I and yielded a value of about  $-50 \text{ cm}^{-1}/\text{kbar}$ .

In order to understand the rapid decrease of the frequency factor ( $\alpha$ ) with increasing pressure (Table I), a more complete description was considered based on the energy level diagram shown in Fig. 1 and yielded

$$\alpha = (1 - \beta) \frac{P_{\text{cd}}^{\text{nr}}}{P_{\text{df}}^{\text{r}}} \quad (2)$$

where  $P_{\text{df}}^{\text{r}}$  and  $P_{\text{cd}}^{\text{nr}}$  are the radiative  $5d(1) \rightarrow 4f$  transition rate and the nonradiative rate of recapturing the delocalized electron from the conduction band to the  $5d(1)$  state, respectively.  $\beta$  is the branching ratio of the recapture rate ( $P_{\text{cd}}^{\text{nr}}$ ) to the total dissipation rate of the delocalized  $5d$  electron. The total dissipation rate includes the recapture rate ( $P_{\text{cd}}^{\text{nr}}$ ), the radiative band-band recombination rate ( $P_{\text{cv}}^{\text{r}}$ ), and the non-radiative relaxation rate between the conduction band and the ground  $4f$  state of  $\text{Ce}^{3+}$  ( $P_{\text{cf}}^{\text{nr}}$ ). From Eq. (2), we can see that the frequency factor ( $\alpha$ ) depends on the branching ratio ( $\beta$ ), the recapture rate ( $P_{\text{cd}}^{\text{nr}}$ ), and the radiative  $5d(1) \rightarrow 4f$  rate ( $P_{\text{df}}^{\text{r}}$ ).

The radiative  $5d(1) \rightarrow 4f$  transition rate ( $P_{\text{df}}^{\text{r}}$ ) is generally expected to increase with pressure primarily because of the pressure-induced increase in crystal-field strength.<sup>18</sup> The increased  $5d(1) \rightarrow 4f$  transition rate contributes to a decrease in  $\alpha$ .

$\beta$  can in principle vary from 0 to 1. When a material is changed from a direct band structure to an indirect band structure, the radiative band-band recombination rate should be changed significantly by several orders of magnitude. We expect that the branching ratio ( $\beta$ ) is close to zero before the structural transformation and significantly increases in the high-pressure phase, depending on the ratio of  $P_{\text{cf}}^{\text{nr}}/P_{\text{cd}}^{\text{nr}}$ .

The recapture rate ( $P_{\text{cd}}^{\text{nr}}$ ) is related to a difference in the electron-phonon coupling strength of an electron in the conduction band relative to the  $5d(1)$  state of  $\text{Ce}^{3+}$ . This rate should be strongly influenced by the direct-indirect change in the band structure of the host lattice because the electron-phonon coupling is much different for an electron in a direct

band edge relative to an indirect band edge. In other words, in the configurational coordinate model,<sup>19</sup> the Huang-Rhys coupling constant ( $S$ ) relative to the emitting  $5d(1)$  state of  $\text{Ce}^{3+}$  is significantly different for a direct band edge relative to an indirect band edge. We expect that this effect leads to a large reduction of the recapture rate ( $P_{cd}^{nr}$ ) as the direct  $\text{Lu}_2\text{S}_3$  is transformed to an indirect  $\text{Lu}_2\text{S}_3$  host with pressure.

The overall combination of the three contributions leads to the observed decrease in the frequency factor ( $\alpha$ ).

## V. CONCLUSIONS

We have used pressure to widely tune the activation energy between the conduction band edge of  $\text{Lu}_2\text{S}_3$  and the emitting  $5d$  state of  $\text{Ce}^{3+}$ . As a result, we have observed

significant changes in the  $d \rightarrow f$  luminescence properties in  $\text{Ce}^{3+}:\text{Lu}_2\text{S}_3$ . Most notably, we have observed a strong decrease in  $\text{Ce}^{3+}$  luminescence intensity with increasing pressure due to an electron crossover of the conduction band edge of the host lattice with the emitting  $5d(1)$  state of  $\text{Ce}^{3+}$ . The strong variation of the  $\text{Ce}^{3+}$  luminescence intensity has provided a unique opportunity to demonstrate the photoionization mechanism proposed by Yen.<sup>7</sup>

## ACKNOWLEDGMENTS

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