



Temperature-dependent luminescence of cerium-doped ytterbium oxyorthosilicate

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Abstract

We have measured optical absorption and radioluminescence of $\text{Yb}_{1.999}\text{Ce}_{0.001}\text{SiO}_5$ (YbSO) and found it to be a very poor phosphor. This is in striking contrast to Lu-, Y-, and Gd-based oxyorthosilicates, which are characterized by very strong Ce^{3+} emission. The absence of luminescence in YbSO is due to quenching of the Ce^{3+} emission via an $[\text{Yb}^{2+}-\text{Ce}^{4+}]$ charge-transfer mechanism. Extremely weak band emission observed in YbSO is attributed to transitions connecting the $(\text{Yb}^{2+}-h^+)$ charge-transfer state to the two levels of the $\text{Yb}^{2+} 4f^{13}$ configuration. Optical absorption shows the usual bands due to Ce^{3+} absorption with a band edge near 260 nm. The RL emission spectrum consists of a well-resolved band near 500 nm and an additional band in the region 260–300 nm. The exact position of the latter band cannot be determined due to concomitant Ce^{3+} absorption. At room temperature the YbSO RL emission is ca. six orders of magnitude weaker than $\text{Lu}_2\text{SiO}_5 : \text{Ce}$ (LSO) emission. Maximum intensity in the interval 8–300 K occurs near 40 K and is ca. four orders of magnitude weaker than LSO emission. The YbSO band emission is thermally quenched with increasing temperature (40–300 K), consistent with classical theory predictions. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of efficient inorganic scintillators has been driven by applications in medical imaging and industrial measuring systems [1]. Myriad host lattices containing rare-earth ions as luminescent activators have been investigated because the 4f–5d transitions of these ions are parity-allowed yielding fast (\sim ns) optical transitions that

are highly desirable in many applications. Fast relaxation is attributable to the ion's favorable energy configuration within the host lattice whereby the 4f and lowest 5d levels reside within the normally forbidden crystalline band gap. Transfer of energy from radiation-induced electron–hole pairs to the luminescent ion is usually quite efficient, although quenching due to nonradiative electronic transitions may limit the overall luminescence efficiency of the phosphor [2].

Much attention has been recently devoted to scintillation properties of the cerium-doped

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rare-earth oxyorthosilicates Lu_2SiO_5 [3,4], Gd_2SiO_5 [5,6] and Y_2SiO_5 [7] as well as lutetium aluminate LuAlO_3 [8] and yttrium aluminate YAlO_3 [9]. Each of these materials exhibits excellent quantum efficiency at room temperature with emission in the 400 nm region, which is typically associated with Ce^{3+} electronic transitions. Interestingly, partial substitution of Yb^{3+} for Y^{3+} in the oxyorthosilicate lattice results in a material that luminesces weakly if at all at room temperature. Presumably, the quenching of luminescence is due to crossing of the ground- and excited-state energy levels or to electron charge-transfer as discussed in Ref. [2] or to both. It has been previously demonstrated that substitution of Yb for Lu in cerium-activated LuPO_4 quenches the luminescence by the latter mechanism, and the simultaneous presence of Yb and Ce is always deleterious to scintillator efficiency [10]. Based on preliminary cluster model calculations it has been recently suggested that $\text{Yb}_2\text{SiO}_5 : \text{Ce}$ (YbSO), which exhibits at best only weak luminescence at room temperature, might luminesce much more strongly at lower temperature [11]. Intrigued by this possibility we undertook an investigation of the temperature-dependent radioluminescence of this cerium-activated orthophosphate.

2. Experimental technique

A single-crystal specimen of $\text{Yb}_{1.999}\text{Ce}_{0.001}\text{SiO}_5$ was obtained from Litton Airtron, Inc., and used in the as-received condition for radioluminescence (RL) and optical absorption measurements. A small sample ($2 \times 6 \times 10 \text{ mm}^3$) was mounted onto an aluminum sample holder of a continuous-flow liquid helium cryostat and irradiated with 25 keV effective-energy X-rays (50 kV, 40 mA) to produce luminescence. X-radiation entered the evacuated ($\sim 10^{-6}$ Torr) cryostat through a beryllium window and the RL was collected by an optical fiber, which was positioned at an angle of 90° with respect to the X-ray beam. The collected RL was transmitted via the fiber to the entrance slit of a $\frac{1}{4}$ m monochromator, whose output was detected by a charge-coupled device camera, the entire system comprising an optical multichannel analyzer

(OMA). Data were collected at 10 K intervals from 20 to 120 K, with additional data taken at 8, 200, and 290 K. A temperature controller maintained the sample temperature to within $\pm 1^\circ$ of the set point. Due to the relative weakness of the RL signals, OMA integration times of 6 min were required to collect sufficient data at each temperature. X-ray excitation occurred only during this time interval, and with an exposure rate at the sample position of 200 R/s this corresponded to total exposure of 7.2×10^4 R at each temperature.

Radioluminescence spectra for each temperature were obtained in the spectral region 200–800 nm utilizing monochromator entrance and exit slit widths of 1000 μm . The spectral resolution was ca. 1 nm as determined by a separate measurement of the 365 nmHg line. All spectra were corrected for the nonlinear response of the spectrophotometer, plotted in energy units, and fitted with Gaussian profiles. Relative intensities of emission peaks were extracted from the fitted data and plotted as a function of temperature.

A Cary 5E spectrophotometer was used for optical absorption measurements on YbSO and $\text{Lu}_2\text{SiO}_5 : \text{Ce}$ (LSO), all measurements being made at room temperature. The samples were measured in the as-received state without further optical polishing and appeared to be free of surface irregularities. The LSO sample contained 0.25% Ce and was kindly provided by Dr. C. Melcher of CTI, Inc.

3. Results

The well-known optical absorption of LSO, initially measured by Melcher and Schweitzer [4], exhibits at least four bands between 360 nm and the band edge at 188 nm (6.59 eV). These arise from electronic transitions between the Ce^{3+} 4f ground state and the crystal-field split 5d levels. Similar absorption is found in YbSO although the band edge appears at 260 nm (4.77 eV), reduced by 1.82 eV from that of LSO. This substantial shift results from the considerably larger association energy of Yb as compared with Lu, and, consequently, permits observation of only two of the Ce^{3+} absorption bands, as shown in Fig. 1. The strongest absorption occurs near 355 nm.

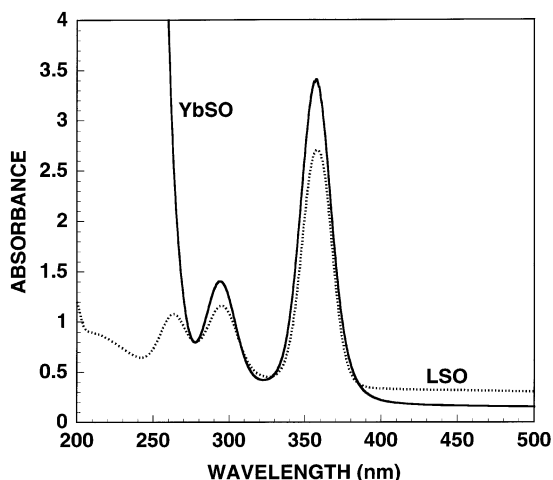


Fig. 1. Optical absorption of YbSO and LSO. Note the onset of band edge absorption in YbSO near 4.77 eV (260 nm).

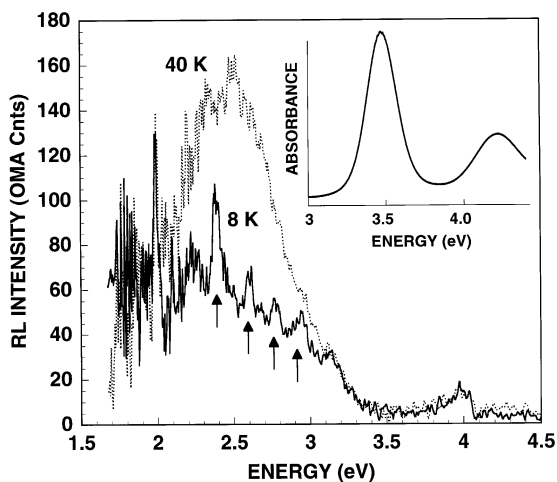


Fig. 2. Radioluminescence of YbSO measured at 8 and 40 K. The upward arrows in the 8 K spectrum correspond to unidentified impurities and are absent at higher temperature. The inset shows the pertinent portion of the YbSO optical absorption of Fig. 1 plotted on the same energy scale as the RL spectrum. Note the rise in the RL spectrum near 4 eV and the corresponding increase in optical absorption at this energy.

In Fig. 2 we show RL emission from YbSO taken at 8 and 40 K. At the lowest temperature both band and line emissions (indicated by the upward arrows) are evident; however, for $T \geq 20$ K only the band emission is observed. The spectral position of

maximum band intensity occurs near 2.5 eV (500 nm) and is weakly temperature dependent. In addition there is evidence for another band centered at energy higher than 4 eV; it is only partially resolved due to strong reabsorption by Ce^{3+} ions of the RL emission. The inset of Fig. 2 shows YbSO optical absorption of Fig. 1 plotted on the same energy scale as the RL emission. Note the rise in RL emission near 4 eV that occurs in concert with enhanced absorption near 4.2 eV. A similar situation has been observed in $\text{YbPO}_4:\text{Ce}$ (YbPO) [10]. In this study it was shown that RL emission consists of bands at 300 and 430 nm, attributable to charge-transfer transitions of the Yb ion, and further that the latter emission band was not resolved due to absorption of RL emission by Ce^{3+} ions. Similar emission is expected from YbSO thereby supporting our conclusion that a second RL emission band exists above about 4 eV.

RL emission obtained at 20 and 30 K consists solely of the band spectrum with an intensity that is approximately temperature independent. However, at 40 K the intensity abruptly increases to the maximum value observed at any temperature. With further increase of temperature the RL intensity decreases and is extremely weak for all temperatures above about 100 K. Representative data are shown in Fig. 3. Note that RL emission occurring below about 2 eV becomes quite noisy due to the reduced sensitivity of the OMA and can be ignored.

To aid our understanding of the measured RL spectra we fitted all data except the 8 K spectrum, which contained unidentified line emission, with both Gaussian and Voigt line shapes. There were only minor differences in the goodness of fit between Gaussian and Voigt profiles and therefore we chose to present only the Gaussian results. Two Gaussians were required to fit the spectra, a main band with maximum at 2.45 eV, and a very weak, broad band with maximum at 3.20 eV, as shown in Fig. 4 for the 40 K emission. The exact spectral position of the main band varies slightly with temperature whereas the weak band position appears to be temperature independent. This latter band is attributable to either an artifact or to extremely weak Ce^{3+} emission. As discussed below, we suggest that the dominant emission in YbSO is due to

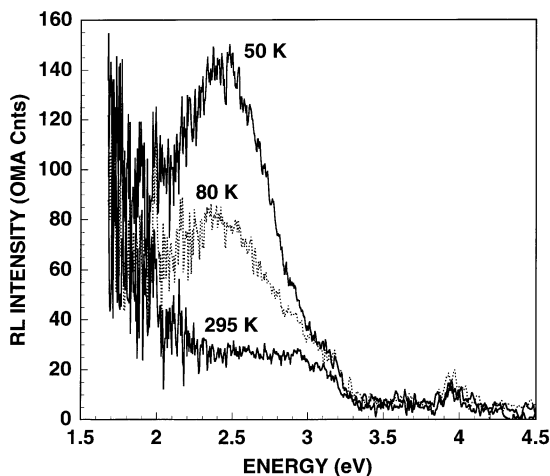


Fig. 3. RL spectra of YbSO measured at three temperatures to illustrate the temperature-dependent behavior. The enhanced noise below 2 eV is due to decreased sensitivity of the OMA. All spectral data have been corrected for nonlinearities in the spectrophotometer response.

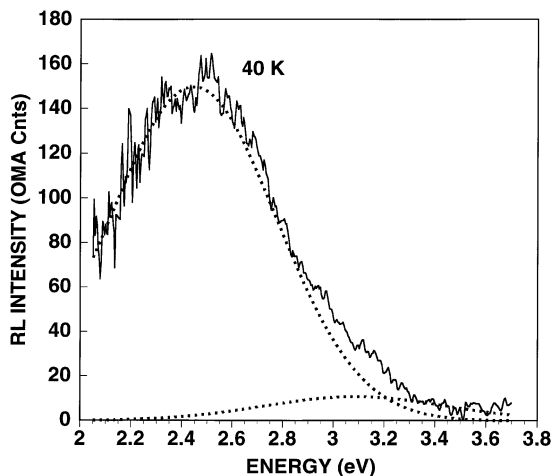


Fig. 4. Main emission band of YbSO fitted with a Gaussian profile. The broad weak emission centered near 3.2 eV is due to either an artifact or weak Ce^{3+} emission. Note the enhanced energy scale relative to Figs. 2 and 3.

Yb rather than Ce. Characteristic Yb-based emission consists of two bands: a well resolved one centered near 2.45 eV, and another that is partially obscured by the strong Ce^{3+} absorption; its peak

position is bracketed by the observed initial rise near 4 eV in the RL spectrum (see Fig. 2) and the absorption band edge at 4.77 eV (see Fig. 1).

From the Gaussian-fitted data we extracted the temperature dependence of the 2.45 eV band intensity and present the result in Fig. 5. The solid circles are fitted intensities and the error bars are statistical ones derived from the Gaussian fits. The dashed line represents expected temperature-dependent behavior for thermal quenching of luminescence and will be discussed in the next section. Note the abrupt deviation from the expected intensity for $T < 40$ K. This anomalous behavior was further investigated by measuring the intensity as the temperature increased, and subsequently decreased; it was found to be completely reversible.

From Fig. 5 we see that the maximum RL intensity of YbSO is approximately 160 OMA counts. For comparison purposes we measured LSO under similar conditions and found the intensity to be more than four orders of magnitude greater at low temperature and more than six orders of magnitude greater at room temperature, thus confirming the earlier conclusion that cerium-doped YbSO is at best a very poor phosphor at all temperatures.

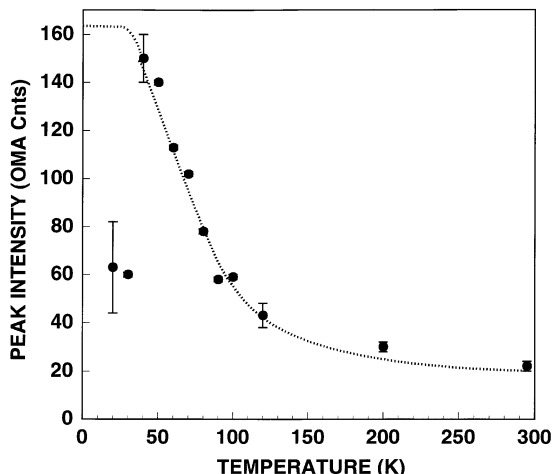


Fig. 5. Temperature dependence of the 2.45 eV band intensity in YbSO. The dashed line represents the expected temperature dependence according to classical quenching theory. Deviation from the expected behavior occurs below 40 K and may be associated with thermally activated hole localization within the $[\text{Yb}^{2+}\text{-h}^+]$ charge-transfer state.

4. Discussion

Analysis of the experimental results obtained in the present work provides important information on the luminescence process in orthosilicates containing both Ce and Yb ions. In contrast to the excellent luminescent properties of cerium-doped LSO and YSO, our results clearly demonstrate that replacement of either Lu or Y by Yb essentially quenches the luminescence, and supports previous conclusions regarding luminescence efficiency in cerium-doped orthophosphates [10], viz., that nonradiative decay of the $[\text{Yb}^{2+}-\text{Ce}^{4+}]$ charge-transfer state mutually quenches the luminescence in YbSO.

Aside from the line spectrum, which is seen only at 8 K and attributed to unknown low-level impurities, the main emission from YbSO consists of a band with a maximum near 500 nm, and a second band with maximum below 300 nm that cannot be fully observed due to Ce^{3+} absorption. This is similar to the emission observed in $\text{YbPO}_4:\text{Ce}$ (YbPO) where bands at 430 and 300 nm (exact position depends on Ce content) [10] have been assigned to transitions between the charge-transfer state, composed of divalent ytterbium and a bound valence hole ($\text{Yb}^{2+}-\text{h}^+$), and the two levels (${}^2\text{F}_{7/2}$ and ${}^2\text{F}_{5/2}$) of the $\text{Yb}^{2+} 4f^{13}$ configuration [12]. From the large energy separation of the two emission bands in YbSO (~ 2 eV) relative to LSO (~ 0.25 eV), which is dominated by Ce^{3+} emission with bands at 390 and 425 nm, we conclude that weak band emission in YbSO is due to Yb charge-transfer rather than Ce^{3+} de-excitation. Optical absorption measurements show the YbSO band edge to be near 260 nm (4.77 eV), whereas the partially resolved band emission maximum occurs below 300 nm, suggesting that the unrelaxed charge-transfer state of Yb lies ca. 0.5 eV below the YbSO band edge.

The temperature dependence of the Yb emission, as measured by the peak intensity of the 2.45 nm band and shown in Fig. 5, is well described by the theory of thermal quenching [13]. For competition between radiative and nonradiative transitions within a luminescence center, the classical theory predicts that the temperature-dependent intensity can be described by the expression

$$I(T) = \frac{I_0}{1 + a e^{-E/kT}}, \quad (1)$$

with constant a , activation energy E and Boltzmann constant k . A fit of Eq. (1) to the experimental data is shown as the dashed line of Fig. 5 with parameters $I_0 = 163.69$ OMA counts, $a = 16.31$, and $E = 18.9$ meV. Excellent agreement between theory and experiment strongly suggests that the decrease in RL intensity with increasing temperature is due to thermal quenching of the $(\text{Yb}^{2+}-\text{h}^+)$ to Yb^{2+} ground-state transition.

Although strong Ce^{3+} RL is observed in LSO it is essentially absent in YbSO; instead, weak Yb emission constitutes RL in YbSO. Wojtowicz et al. [10] observed a similar behavior in orthophosphate scintillators. For example, they found that $\text{LuPO}_4:\text{Ce}$ showed strong Ce^{3+} emission with peaks at 334 and 360 nm, but, surprisingly, the emission was absent in YbPO_4 . They attributed the lack of emission to a mechanism known to occur in other rare-earth combinations, viz., codoping with Ce and Eu [14]. When one of the ions (e.g., Eu^{3+}) has a high association energy for an additional electron, the activator (Ce^{3+}) emission can be severely quenched by the formation of an intermediate charge-transfer state $[\text{Ce}^{4+}-\text{Eu}^{2+}]$, which decays nonradiatively. Similarly, Yb^{3+} has a high association energy for an additional electron and it likely forms a charge-transfer state with Ce $[\text{Ce}^{4+}-\text{Yb}^{2+}]$. This state lies between the ground and excited states of Ce^{3+} and constitutes the non-radiative decay mechanism in YbSO. An analogous process has been proposed to explain the quenching of Ce^{3+} emission in CeF_3 [15]. Therefore, the present data suggest that the lack of Ce emission in YbSO is due to mutual quenching by formation of a charge-transfer state.

Finally, we note an abrupt increase in Yb^{2+} emission intensity as the temperature increases from 30 to 40 K (see Fig. 5). Although the nature of this thermally activated mechanism is at present unknown, we speculate that it is associated with the formation of the $(\text{Yb}^{2+}-\text{h}^+)$ charge-transfer state, which involves localization of a hole in the valence band. Mott and Stoneham [16] have shown that formation of molecular polarons or self-trapped excitons in an insulator requires that a potential energy barrier be surmounted by the configuration coordinate. This process is expected to be temperature dependent.

5. Conclusions

In summary, we conclude that YbSO is a poor phosphor owing to quenching of the Ce luminescence via a $[\text{Yb}^{2+}-\text{Ce}^{4+}]$ charge-transfer state. The predominant luminescence observed in this material is weak band emission attributed to transitions connecting the $(\text{Yb}^{2+}-\text{h}^+)$ charge-transfer state to the two levels ($^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$) of the $\text{Yb}^{2+} 4\text{f}^{13}$ configuration. The RL emission spectrum consists of a well-resolved band near 2.45 eV, and a second band that is only weakly evident because of the strong absorption of Ce^{3+} ions. The maximum of the latter band is bracketed between 4 and 4.77 eV. Lu with its filled 4f shell cannot form a charge-transfer state with Ce, which has one electron in its 4f shell, and thus mutual quenching does not occur. Maximum YbSO emission, dominated by $(\text{Yb}^{2+}-\text{h}^+)$ de-excitation, occurs near 40 K and is ca. four orders-of-magnitude weaker than LSO emission, which is dominated by Ce^{3+} transitions. The $(\text{Yb}^{2+}-\text{h}^+)$ band emission is thermally quenched with increasing temperature and is consistent with predictions of classical theory. Interestingly, at 8 K the YbSO emission is less than half its value at 40 K. This abrupt increase which occurs between 30 and 40 K may be associated with the temperature-dependent formation of the localized hole state comprising the $(\text{Yb}^{2+}-\text{h}^+)$ charge-transfer state.

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