

Phosphorescence and thermoluminescence of uv-irradiated CaO powders at temperatures from 120 to 350 K

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Long-lived phosphorescence and thermoluminescence (TL) from uv-irradiated CaO powders under high vacuum are observed at low temperatures. The emission spectra of phosphorescence and TL have a peak at about 3.0 eV. On the basis of the phosphorescence decay curves, TL glow curves, and ESR data, a plausible emission mechanism is discussed in terms of thermally assisted tunneling recombination between electron traps near the surfaces and hole traps.

1. Introduction. A considerable number of studies have been carried out on the luminescence of alkaline-earth oxides due to bulk defect centers or impurity ions. In thermochemically reduced (TCR) CaO and MgO crystals, long-lived ($\sim 10^2$ s) phosphorescence and thermoluminescence (TL) were observed below room temperature (RT).¹⁻³ These luminescent processes were clearly understood on the basis of the F -center luminescence, which was caused by the recapture of a thermally released electron from H^{2-} impurity ions into an F^+ center to produce the 2.1- and 2.3-eV emission bands in CaO and MgO, respectively. On the other hand, absorption in alkaline-earth oxide powders due to surface excitons was observed with energies smaller than the bulk band gaps, ~ 4.4 – 5.7 eV, by use of uv-visible reflectance spectroscopy.⁴ The short-lived (< 1 ms) photoluminescence was also observed at 3.0 and 3.2 eV for CaO and MgO powders, respectively, when excited by the uv light.⁵ This emission process was explained as the radiative decay of surface excitons. In β -irradiated CaO and MgO powders, a low-temperature TL was observed in vacuum, and an F -type center on a surface and a V -type center in bulk, F_s^+ and V^- , respectively, took part in the emission process through a radiative tunneling recombination mechanism based on electron-spin resonance (ESR) measurements.⁶⁻⁸ More recently, we reported the long-lived phosphorescence and TL of uv-irradiated MgO powders below RT and their quenching induced by O_2 gas exposure.⁹ In this work, we present the phosphorescence and TL of uv-irradiated CaO powders under high vacuum at low temperatures from 120 to 350 K. The role of the surface centers on the luminescence phenomena is discussed in relation to the thermal decay of F_s^+ ESR signals, and the decay kinetics of the luminescence is examined by performing a numerical analysis based on a thermally assisted tunneling recombination mechanism.

2. Experimental. A CaO powder of "Specpure" grade from Johnson Matthey Chem. Ltd. was preheated at 1200 K in a quartz tube (4 mm in diameter) at a base pressure of 2×10^{-8} Torr. Temperatures were adjusted to between 120 and 350 K, using a cooled N_2 gas flow apparatus with a heater outside the quartz tube. The sample was irradiated by uv light (a low-pressure Hg lamp, ~ 4.9 eV) for 10 min in the temperature range 130–350 K. Phosphorescence was measured at a constant temperature within ± 0.2 K over two decades of time from 5 to

2000 s, and TL glow curves were recorded over the temperature range 120–350 K at a heating rate (β) of 0.25 K/s by using a thermoelectrically cooled Hamamatsu R375 photomultiplier tube. Luminescence spectra were measured with use of a grating monochromator (Bausch & Lomb) without the correction for the spectral response. Optical bleaching was carried out with suitable light from a 150-W xenon lamp through glass cutoff filters. ESR spectra were measured at temperatures from 170 to 300 K with use of a JEOL-PE3X X -band spectrometer. g values and the concentration of paramagnetic centers in the sample were calibrated by standard ESR lines of Mn^{2+} in MgO powders and 1,1'-diphenyl-2-picrylhydrazyl (DPPH) in benzene. After each cycle of measurements, the sample was heated up to 1200 K to retain the initial surface states.

3. Results and discussion. The long-lived phosphorescence was observed following uv irradiation of CaO powders, and decay curves at temperatures from 130 to 350 K are shown in Fig. 1 on logarithmic scales. Relative phosphorescence intensities after 100 s of uv cessation decreased gradually above 190 K, and the ratios of the intensities at 190, 225, 250, 280, and 350 K were approximately 1:0.7:0.5:0.3:0.1. The phosphorescence decay rate is not so dependent on uv irradiation temperature (T_{irra}). The slope of decay curves below 190 K is close to -1 over more than two decades in time, and becomes slightly steeper above 225 K for more than ~ 100 s (~ -1.25 at 350 K). Thus, the curves can be fitted neither as a simple exponential decay nor as a power law, while the long-lived F -center luminescence of TCR CaO and MgO crystals followed a second-order decay kinetics with the convenient lifetime of $\sim 10^2$ s.^{2,3} A similar t^{-1} decay of phosphorescence from β -irradiated CaO powders at 77 K (Ref. 8) and from uv-irradiated MgO powders at temperatures from 140 to 300 K was observed.⁹ The phosphorescence decay following approximately t^{-1} and the nearly temperature-independent decay rate are strongly suggestive of a radiative tunneling process between trapped charges and recombination centers.^{10,11} The slight increase of the slope above 225 K may be due to a thermally activated process, which will be discussed later.

After uv irradiation at temperatures of 150, 165, 190, 225, 250, and 280 K and subsequent cooling to 120 K, TL glow curves are observed as shown in Fig. 2 (curves a – f , respectively). With T_{irra} increasing from 150 to 280 K,

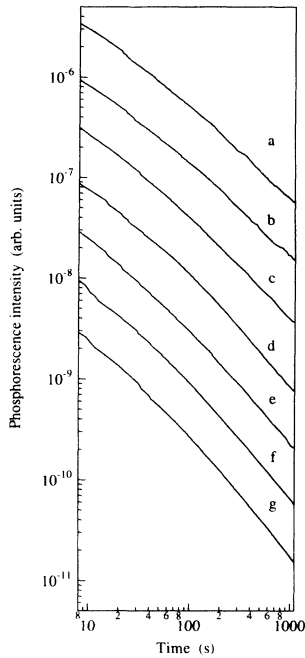


FIG. 1. Log-log plots of the phosphorescence of uv-irradiated CaO powders for 10 min at 130 K (curve a), 165 K (b), 190 K (c), 225 K (d), 250 K (e), 280 K (f), and 350 K (g). The curves are displaced arbitrarily along the vertical axis for convenient graphical presentation in this figure and the next one.

the TL peak intensity decreases by a factor of 20 and the peak temperature (T_p) shifts to higher temperatures from 170 to 300 K. The increase of T_{irra} 's affects only the rising side of the TL glow curves. For the TL glow curve at $T_{\text{irra}} = 150$ K, the TL intensity increases more rapidly and decreases more slowly than T_p . Such an asymmetric line shape of the glow curve is not thought to originate

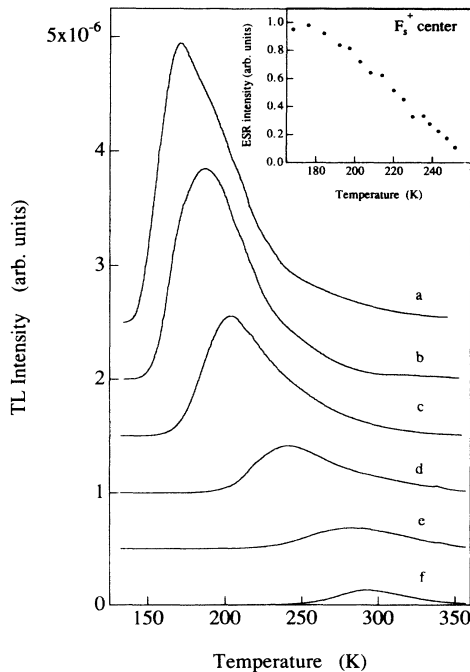


FIG. 2. TL glow curves of CaO powders after uv irradiation for 10 min at 150 K (curve a), 165 K (b), 190 K (c), 225 K (d), 250 K (e), and 280 K (f). Heating rate is about 0.25 K/s. Inset: Thermal decay of F_s^+ ESR signal after uv irradiation at 170 K for 10 min.

from a thermally activated process of a single trap obeying a first-order decay law. The thermal activation energies of the TL (E_a 's) were estimated by the initial rise method to be 0.39, 0.40, 0.35, 0.37, 0.33, and 0.38 eV for $T_{\text{irra}} = 150, 165, 190, 225, 250,$ and 280 K, respectively, indicating that the E_a 's are almost independent on both T_{irra} and T_p . These features were noted in the TL of calcite, and the emission process was explained by a thermally assisted tunneling recombination between the traps with the same E_a , rather than a thermal ionization of charges from the traps with a distribution of E_a 's.¹⁰ By using a modified Arrhenius plot applied to thermal desorption (TD) kinetics,¹² where the same types of kinetic equations are expected between TL and TD mechanisms, a suitable kinetic order of 1 or 2 could not be obtained in the present TL. The TL process observed in TCR CaO crystals, where substitutional H^{2-} ions act as electron traps, may be excluded because of the different T_p 's of TL at 90 and 290 K with E_a 's of ~ 0.1 and 0.7 eV, respectively.¹ Based on ir measurements, no surface H or OH group on CaO powders was detected after the high-temperature (~ 1100 K) and high vacuum ($< 7 \times 10^{-7}$ Torr) pretreatment.¹³ Thus, a hydrogen concentration is suggested to be very low in CaO powders under the present pretreatment.

After uv irradiation at 170 K, an ESR spectrum of a slightly asymmetrical peak with $g = 1.9988$ and $\Delta H = 2.3$ G was observed. This g value is very close to that of F_s^+ centers on β -irradiated CaO powders ($g = 1.998$ and $\Delta H = 2.5$ G),⁷ and so we attributed this signal to F_s^+ centers on CaO surfaces. The concentration of the signal was estimated to be $\sim 5 \times 10^{17}$ spins/g. A broad, weak ESR signal with $g_{\perp} = 2.07$ and $g_{\parallel} = 2.00$ was also observed after uv irradiation, which was assigned to be bulk V^- centers ($g_{\perp} = 2.072$ and $g_{\parallel} = 2.004$),⁷ while the possibility of surface O^- ions (or V_s^- centers) was not excluded. Although traces of ESR lines of Mn^{2+} and Cr^{3+} impurity ions were observed, the intensities of these signals were not affected by uv irradiation. With heating up to RT, the signal intensity of F_s^+ centers at the temperatures decreases gradually and almost disappears at RT, as shown in Fig. 2 (inset), and that of V^- centers decreased similarly. ESR intensities observed at 170 K following an appropriate annealing at higher temperatures showed the similar thermal decay. Thus, a good correlation between the F_s^+ (and V^-) decay and the TL glow curve for the same T_{irra} was obtained. Based on TL and ESR measurements of β -irradiated CaO powders at 77 K, Aristov *et al.* observed TL at $T_p = 120$ K with $E_a \sim 0.1$ eV and isothermal decay of ESR signals for F_s^+ and V^- centers obeying $N(t) \propto -\ln t$, where $N(t)$ is the number of trapped centers.^{7,8} They explained the emission process as the thermally assisted tunneling recombination of an electron at an F_s^+ center and a hole at a V^- center. Accordingly, the present TL observed at low temperatures can be explained by the tunneling recombination mechanism between electron and hole pairs in distant F_s^+ and V^- centers. The difference of E_a 's (0.1 eV reported by Aristov compared with the present one, ~ 0.37 eV) might be due to the tunneling process with a small E_a caused by

the lower temperature β irradiation ($T_{\text{irra}} = 77$ K), although this is not confirmed under the present experimental conditions. After optical bleaching with $\lambda > 600$ nm for 200 s at 200 K, the phosphorescence and TL intensities decreased to 60% of those without bleaching. In CaO crystals, the optical-absorption band of V^- centers is known to be near 1.9 eV.¹⁴ Thus, it is suggested that V^- centers take part in the luminescent process, and holes optically released into the valence band may bleach the phosphorescence and TL. Another possibility of the bleaching is due to optical absorption of F_s^+ centers at 1.9 eV on CaO powders,¹⁵ and electrons may be released into the conduction band to result in the bleaching. The precise bleaching processes, however, are not known. Our preliminary results of O_2 exposure of uv-irradiated CaO powders indicated that both phosphorescence and TL are irreversibly quenched at low temperatures. This fact implies that O_2 molecules interact with surface centers on uv-irradiated CaO surfaces through a charge-transfer process to form chemisorbed O_2^- molecules, as observed on γ -irradiated CaO powders.¹⁶

In order to clarify the decay kinetics of the luminescence, a calculation based on a model of a radiative tunneling mechanism was carried out including a thermally assisted process. According to Williams *et al.*,¹¹ the radiative recombination rate between an electron and a hole trapped on a donor and an acceptor, respectively, is given by

$$W(r) = W_{\text{max}} \exp(-r/R), \quad (1)$$

where r is the distance of the electron-hole pair, R is one-half the donor Bohr radius, and W_{max} is a temperature-independent constant. By assuming that the concentration of acceptors N_a is in excess compared with that of the donors N_d , the phosphorescence intensity at time t , $I(t)$, is

$$I(t) = -\frac{d}{dt} \langle Q(t) \rangle, \quad (2)$$

where

$$\langle Q(t) \rangle = \exp \left\{ 4\pi N_a \int_0^\infty (e^{-W(r)t} - 1) r^2 dr \right\} \quad (3)$$

is the survival probability of an electron on a donor surrounded by randomly distributed acceptors at time t . For the thermally assisted tunneling case, the rate constant is supposed to contain the usual Boltzmann factor, and the decay rate increases through this term.¹⁰ As proposed by Aristov and Parmon,¹⁷ the rate W is temperature dependent so that

$$W(r, T) = W_{\text{max}} \left\{ 1 + \frac{\nu}{W_{\text{max}}} \exp \left[-\frac{E}{kT} \right] \right\} \exp \left[-\frac{r}{R} \right], \quad (4)$$

where ν is a frequency factor and E a thermal activation energy. Phosphorescence decay curves were calculated for $N_a \gg N_d$ by using $W(r, T)$ with $E = E_a = 0.37$ eV and Eq. (5) in Ref. 11. Here, we consider that a donor is an F_s^+ center and an acceptor is a bulk V^- center, so that the numerical integration was performed over the hemisphere, and the factor $4\pi N_a$ in Eq. (3) was replaced by $2\pi N_a$. The upper limit was chosen to be $r/R = 150$

(defined as ρ , in Ref. 11). Calculated decay curves for $T_{\text{irra}} = 100$ –350 K are shown in Fig. 3(a). The fitting parameters were chosen to be $W_{\text{max}} = 5 \times 10^3$ s⁻¹, $\nu = 1.2 \times 10^{15}$ s⁻¹, and $N_a R^3 / 2 (= n) = 8 \times 10^{-5}$, where the initial distribution of charged traps is assumed to be temperature independent. The value of ν is larger than the usual one for lattice vibrations ($\sim 10^{13}$ s⁻¹). The slope of the decay curves is close to -1 below 175 K and becomes steeper with increasing T_{irra} (~ -1.3 at 350 K), indicating that the phosphorescence decay is effectively accelerated by thermally assisted tunneling recombination above ~ 200 K. The phosphorescence intensity level at 100 s decreases considerably for $T_{\text{irra}} > 200$ K. Thus, a qualitative agreement between model calculations and experimental data is obtained, while the model gives steeper decay curves than the measurements and the changes of

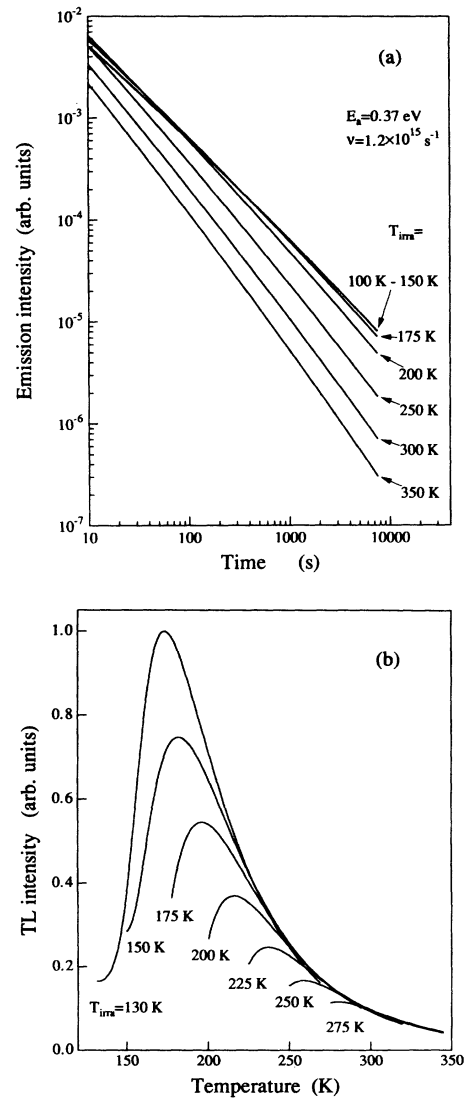


FIG. 3. (a) Log-log plots of calculated decay curves corresponding to thermally assisted tunneling recombination of electrons and holes for the temperature range from 100 to 350 K. (b) Calculated TL glow curves for $T_{\text{irra}} = 130$ –275 K. The fitting parameters are $n = 8 \times 10^{-5}$, $W_{\text{max}} = 5 \times 10^3$ s⁻¹, and $\nu = 1.2 \times 10^{15}$ s⁻¹ with $E_a = 0.37$ eV and $\beta = 0.25$ K/s.

relative intensities with temperature are more marked in the model than in the experiment. The above calculations are based on the assumption of $N_a \gg N_d$. As pointed out by Williams *et al.*,¹¹ in the case of low concentrations or small n values ($n \leq 10^{-4}$), the calculated decay curves for $N_a \gg N_d$ are almost the same as those for $N_a = N_d$ at fixed W_{\max} 's. Since F_s^+ and V^- centers are expected to be formed in nearly equal amounts, the concentration of V^- centers, N_a , may be roughly estimated from that of F_s^+ centers to be $\sim 10^{18}/\text{cm}^3$, and then $R \approx (2n/N_a)^{1/3} \approx 5 \text{ \AA}$, which is similar to the value of electron trapped centers in MgO crystals.¹¹ The same formula, Eq. (5) in Ref. 11, was applied for TL processes with linear heating, $T = T_{\text{irra}} + \beta t$. The calculated TL glow curves for T_{irra} 's from 130 to 275 K are shown in Fig. 3(b) by using the same parameter values obtained for the phosphorescence decay. The TL glow curve at $T_{\text{irra}} = 130 \text{ K}$ shows an asymmetric line shape with $T_p \sim 175 \text{ K}$, which is the characteristic of the TL due to thermally assisted tunneling recombination.⁶ With increasing T_{irra} , a calculated T_p shifts to higher temperature and a TL peak height decreases significantly. These are in qualitative agreement with observation, while the rising side of calculated glow curves is steeper than the measurements. Therefore, the thermally assisted tunneling recombination is the most probably mechanism for the emission process of uv-irradiated CaO powders at low temperatures. For $E_a = 0.1 \text{ eV}$, T_p 's of TL glow curves were below 150 K and phosphorescence decay depended considerably on T_{irra} above 100 K, based on the present model with parameters $n \leq 1 \times 10^{-4}$, $10^0 < W_{\max} < 10^6$, and $\nu > 10^5 \text{ s}^{-1}$. This suggests that the TL at $T_p = 120 \text{ K}$ with $E_a \sim 0.1 \text{ eV}$ obtained from β -irradiated CaO powders^{8,9} is different from the present one.

The emission spectra of the phosphorescence and TL of CaO powders after uv irradiation at 150 K are shown in Fig. 4 (curves *a* and *b*, respectively). By assuming a symmetrical Gaussian shape, the emission band of phosphorescence is at 2.95 eV with a half-width of 0.6 eV, and that of TL is at 3.0 eV with the same half-width. It is possible that the bulk F and F^+ centers do not take part in these luminescent processes, as the present emission bands are different from those of phosphorescence of the F and F^+ centers in TCR CaO crystals (2.1 and 3.35 eV, respectively).^{2,18} In the electronic structure of MgO sur-

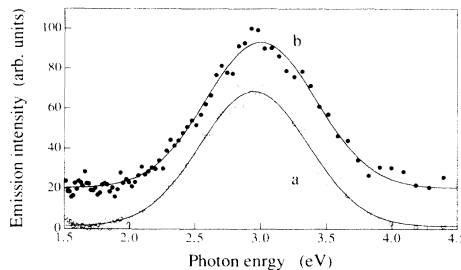


FIG. 4. Phosphorescence and TL emission spectra of uv-irradiated CaO powders for 10 min at 150 K (curves *a* and *b*, respectively).

faces, the 2.3-eV loss peak within the bulk band-gap energy was attributed to surface V^- -type defect centers by use of electron-energy-loss spectroscopy, and an energy level of surface F^- -type centers was suggested to be almost the same as the bulk one.¹⁹ This may be expected for CaO surfaces, so that F_s^+ (or F_s^-) luminescence may be ruled out from the present emission. The radiative decay of surface excitons, which are located at surface cation-anion pairs (M^+-O^- , $M = \text{alkaline-earth atom}$) on alkaline-earth oxide surfaces, was reported to cause short-lived ($< 1 \text{ ms}$) emission bands near 3.2 and 3.0 eV for MgO and CaO powders, respectively, under uv excitation in vacuum.⁵ This emission process, however, may not be operative because of the observed long-lived phosphorescence. Thus, we consider that F_s^+ and V^- centers produced by uv irradiation take part in both phosphorescence and TL processes through the radiative tunneling recombination between an electron and a hole at distant trapped centers. Although the locations of the energy levels of trapping states and the band gap near surfaces are not known with certainty, the energy of emission bands of the phosphorescence and TL at $\sim 3.0 \text{ eV}$ seems to be approximately the energy difference of the electron-hole pairs in the band gap, which may be obtained from the surface band-gap energy [$\sim 3.6 \text{ eV}$ (Ref. 16) or $> 4.2 \text{ eV}$ (Ref. 4)] minus the sum of the binding energies of the donor and acceptor (a rough estimate $\sim 2E_a$). The luminescence may not be associated with transition-metal impurity ions, because concentrations of these ions are very low in the sample ($[\text{Fe}] \sim 1 \text{ ppm}$ and $[\text{Mn}] < 1 \text{ ppm}$),²⁰ and ESR signals of impurity ions, such as Mn^{2+} , were unaffected by uv irradiation.

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²⁰Concentrations as supplied by the manufacturer.