PHYSICAL REVIEW B VOLUME 29, NUMBER 10 15 MAY 1984

Infrared-stimulated luminescence from oxygen vacancies in CaO

G. P. Summers and K. Chakrabarti
Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74078

Y. Chen
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 5 December 1983)

2.1-eV F-center luminescence has been excited in thermochemically reduced CaO at 78 K using low-intensity photons with energy $E < 2.4$ eV, i.e., less than the energy of the main F-center absorption. Thermoluminescence measurements indicate that electrons trapped at substitutional H^{2-} ions are involved in the energy transfer leading to the luminescence.

I. INTRODUCTION

It has recently been shown that the presence of substitutional H^- ions has a profound effect on the luminescence of oxygen-ion vacancies in thermochemically reduced MgO (Refs. 1 and 2) and CaO (Ref. 3). The lifetime of F-center (an oxygen vacancy containing two electrons) luminescence, for example, has been shown to depend on the concentration of H^- ions present.[4] Since a substitutional H^- ion consists of a proton located at an oxygen-vacancy site and surrounded by two electrons, it represents a region of local positive charge in the crystal, which can trap an electron. It is the metastable trapping of optically excited electrons at H^- ions before they are finally captured into the excited state of an F center that leads to the long lifetime of the luminescence near room temperature.

There is evidence that the presence of hydrogen in a sample affects the luminescence from anion vacancies in the thermochemically reduced MgO. The presence of hydrogen tends to favor emission from F centers rather than F^+ centers (oxygen vacancies, each of which has trapped a single and electron). The concentration of hydrogen in MgO can be controlled and crystals containing a range of concentrations of both anion vacancies and H^- ions can be produced. Because of the hygroscopic nature of CaO, however, it has not yet been possible to control the concentration of hydrogen present and thermochemical reduction usually produces crystals containing large concentrations of both anion vacancies and H^- ions.

F centers in CaO absorb at 3.1 eV due to a ${}^1A_{1g} \rightarrow {}^1T_{1u}$ transition.[5] Upon relaxation of the center, an excited ${}^3T_{1u}$ state becomes lowest in energy, and at temperatures below ~ 80 K a radiative ${}^3T_{1u} \rightarrow {}^1A_{1g}$ transition occurs, producing luminescence at 2.1 eV with an intrinsic lifetime of ~ 3 ms.[6] Above ~ 80 K an optically excited F-center electron can be released into the conduction band by means of a thermally assisted transition with an activation energy of 0.1 eV. The released electron is either captured directly by an F^+ center, which leads to 2.1-eV luminescence, or by another trap elsewhere in the lattice.

In this paper we describe the excitation of 2.1-eV F-center luminescence at 78 K in thermochemically reduced CaO using low-energy ($E < 2.4$ eV) radiation. Thermoluminescence measurements indicate that electrons trapped at H^{2-} ions are involved in the energy-transfer process which produces the luminescence.

II. EXPERIMENTAL DETAILS

CaO single crystals were grown by using the arc-fusion process. High-purity-grade $CaCO_3$ starting powder obtained from Mallinckrodt Company was used. Analyses of typical starting material and the resulting crystals have been reported previously.[7,8] The samples were thermochemically reduced at temperatures of ~ 2100 K and at pressures of several atmospheres of calcium vapor. This process resulted in the formation of oxygen-ion vacancies and substitutional H^- ions. The concentration of H^- ions present was estimated from the absorption coefficients α_H of the 880- and 911-cm^{-1} local-mode bands.[9] The concentration of anion vacancies was estimated from the absorption coefficients of the F and F^+ bands, which peak at 3.1 and 3.65 eV, respectively. Three samples were used, two of which (CaO III and CaO IV) were used in previous experiments.[10] These samples were cleaved from adjacent parts of the same ingot. Sample CaO III was electron irradiated to reduce the concentration of H^- ions and to increase the concentration of anion vacancies by proton displacement.[10] The third sample (CaO VI) contained concentrations of H^- ions and anion vacancies close to those of sample CaO IV. Table I shows the characteristics of the samples used.

The photoluminescence experiments were performed in a cryostat, in which the sample was separated from liquid nitrogen by only 0.1 mm of copper. When liquid nitrogen was forced into the cryostat the sample temperature

TABLE I. Characteristics of thermochemically reduced CaO samples.

Sample	n_F (cm^{-3})[a]	n_H (cm^{-3})[b]
CaO III	$>(5\times10^{17})$[c]	2.7×10^{16}
CaO IV	$>(5\times10^{17})$[c]	1.2×10^{17}
CaO VI	$>(5\times10^{17})$[c]	9.4×10^{16}

[a] Calculated using Eqs. (1) and (2) of Ref. 10.
[b] Calculated using Eq. (3) of Ref. 10.
[c] The absorption coefficients at 3.1 and 3.65 eV were too high to be measured.

dropped to ~78 K in a few seconds. Luminescence was excited in the sample using radiation from a 150-W xenon lamp which was dispersed by a 0.25-m Spex monochromator used in conjunction with suitable glass filters. Emission was detected by a thermoelectrically cooled C31034 photomultiplier tube after passing through two interference filters with peak transmission near 600 nm (2.1 eV).

III. RESULTS AND DISCUSSION

Figure 1 shows the results of an experiment using sample CaO VI. The sample was illuminated at room temperature with *F*-center light. When the luminescence reached a maximum the excitation was cut off in ~1 ms. The luminescence intensity dropped rapidly by about an order of magnitude before continuing to decay more slowly by a non-first-order process (Fig. 1). After a few seconds liquid nitrogen was forced into the Dewar and the luminescence was quenched in a matter of seconds. This behavior is indicative of phosphorescence due to charge trapping. After five more minutes the sample was excited with a 40-ms pulse of 1.7 eV (730 nm) radiation with a bandwidth of ~10 nm. A sharp cutoff filter excluded light for $\lambda < 680$ nm. The intensity of the luminescence grew to a peak intensity with a time constant of a few milliseconds. When the excitation was removed the luminescence intensity decayed with a lifetime of ~3 ms before a component with a longer time constant became apparent (Fig. 1). The luminescence could be reactivated in this way many times with only a small drop in peak luminescence intensity. Preliminary experiments indicate that the excitation spectrum for the emission extends beyond 900 nm (1.38 eV) and rises monotonically with increasing energy to 550 nm (2.25 eV). Light with energy greater than 2.25 eV can be absorbed directly into the *F* band. The efficiency of the excitation was comparable for each of the samples studied.

Figure 2 shows the thermoluminescence (TL) glow curves for samples CaO III and CaO IV. The data for sample CaO VI were similar to those for sample CaO IV. These curves were measured over two temperature ranges, 20—300 and 77—400 K, and the two sets of data normalized at 220 K. In each case the sample was cooled to the starting temperature, illuminated with 3.1 eV light for 10 min, and heated at a rate of ~0.1 K s^{-1}. Figure 2 shows that there are several overlapping TL bands in the range 270—350 K. However, the difference in the H^{-} ion concentrations in samples CaO III and CaO IV suggests that the TL band near 320 K is due to the release of electrons from H^{2-} ions. TL occurs when the released electrons are captured into the excited states of *F* centers. Similarly, the difference in the glow curves near 110 K suggests that there might be another electron trap in the samples which is also related to the presence of hydrogen. The fact that there are two intensity-uncorrelated lines in the local mode spectrum of H^{-} ions indicates that these ions might be in two kinds of sites, which are distinguished by different local charge compensators, for example. Separate measurements[3] indicate that thermal release of electrons from H^{2-} ions near room temperature has an activation energy of 0.73 eV and near liquid-nitrogen temperature of ~0.1 eV. It is worth noting that the lifetime of *F*-center luminescence is different in thermochemically reduced and electron-irradiated samples. In thermochemically reduced samples a long-lived phosphorescence component is observed in the range 60—100 K which is not seen in electron-irradiated samples. This result implies that the electron trap(s) causing the low-temperature phosphorescence are introduced by the reduction process and are not otherwise present in the sample.

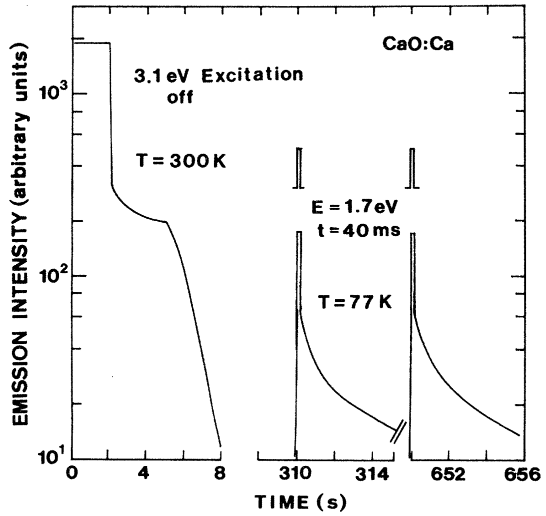

FIG. 1. Luminescence intensity decay in thermochemically reduced CaO (CaO VI). The sample was rapidly cooled from 300 to 77 K at $t = 5$ s. The sample was subsequently illuminated with pulses of low energy, E = 1.7 eV (730 nm) radiation.

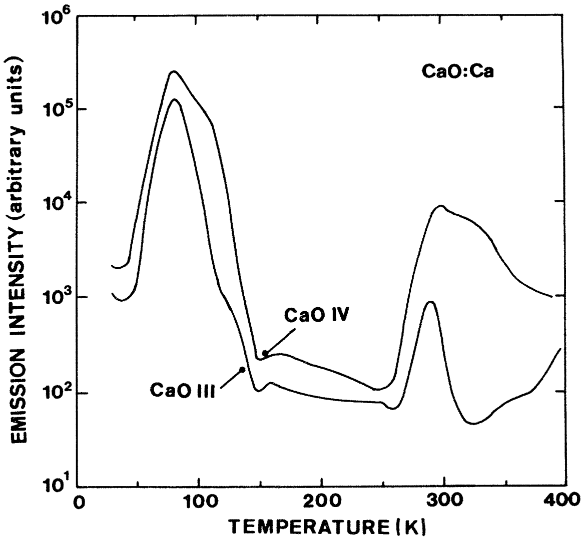

FIG. 2. Thermoluminescence glow curves of thermochemically reduced CaO (CaO III and CaO IV). The data were taken in two temperature ranges and normalized at 220 K.

The TL results suggest that in explaining the data of Fig. 1 we should consider the effect of two main types of electron traps. The deeper of these traps is thermally emptied near room temperature and the shallower is emptied near liquid-nitrogen temperature. As we have discussed above these two traps might both be related to H^- ions. F-center phosphorescence occurs near room temperature when optically excited electrons are captured metastably before returning to F^+ centers. When the sample is rapidly cooled to 77 K, itinerant electrons are frozen into the deeper traps and the phosphorescence is quenched. We suggest that low-energy radiation (e.g., with $E = 1.7$ eV) can excite electrons from these traps into the conduction band, from which some are captured directly into the excited states of F centers. Other released electrons are captured by shallower traps, from which they leak slowly back to F^+ centers. The latter process is similar to that which occurs when F centers are optically excited at 77 K in thermochemically reduced samples. In this model, therefore, the excitation spectrum of the infrared-stimulated emission corresponds to the direct excitation of an electron from an H^{2-} ion into the conduction band. Because of the location of the F-center absorption we have not yet been able to locate the peak of this excitation spectrum experimentally. However, using the formula[12] $E_0/E_t = \epsilon/\epsilon_\infty$ we obtain a rough estimate of 2.5 eV (490 nm) for the optical transition energy E_0, using a value of 0.73 eV for the thermal activation energy E_t. Here we used values of 3.4 and 11.8 for the high- and low-frequency dielectric constants e_∞ and ϵ, respectively. A value for E_0 of 2.5 eV is consistent with the experimental data so far obtained.

There are still several parts of the model suggested above under investigation, but our experimental data confirm that the presence of H^- ions are important in determining the optical properties of thermochemically reduced CaO.

ACKNOWLEDGMENTS

Research at Oak Ridge National Laboratory was supported by the Division of Materials Sciences, U. S. Department of Energy, under contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

---

[1] G. P. Summers, T. M. Wilson, B. T. Jeffries, H. T. Tohver, Y. Chen, and M. M. Abraham, Phys. Rev. B 27, 1283 (1983).

[2] Y. Chen, R. Gonzalez, O. E. Schow, and G. P. Summers, Phys. Rev. B 27, 1276 (1983).

[3] G. P. Summers, K. Chakrabarti, R. Gonzalez, and Y. Chen, Bull. Am. Phys. Soc. 28, 453 (1983).

[4] B. T. Jeffries, R. Gonzalez, Y. Chen, and G. P. Summers, Phys. Rev. B 25, 2077 (1982).

[5] T. M. Wilson and R. F. Wood, J. Phys. Paris Colloq. 37, C7-190 (1976).

[6] L. S. Welch, A. E. Hughes, and G. P. Summers, J. Phys. C 13, 1791 (1980).

[7] Y. Chen, D. L. Trueblood, O. E. Schow, and H. T. Tohver, J. Phys. C 3, 2501 (1970).

[8] M. M. Abraham, C. T. Butler, and Y. Chen, J. Chem. Phys. 55, 3752 (1971).

[9] R. Gonzalez, Y. Chen, and M. M. Mostoller, Phys. Rev. B 24, 6862 (1981).

[10] G. P. Summers, R. Gonzalez, and Y. Chen (to be published).

[11] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), Chap. 5.