PHYSICAL REVIEW B VOLUME 25, NUMBER 3 1 FEBRUARY 1982

Luminescence in thermochemically reduced MgO: The role of hydrogen

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(Received 21 December 1981)

The first unambiguous evidence is presented that H^- ions are the main electron traps responsible for the long-lived phosphorescence observed at 2.3 eV near room temperature in thermochemically reduced MgO.

One of the characteristics of thermochemically reduced[1] MgO and CaO is the long-lived luminescence, or phosphorescence, observed following optical excitation of *F* centers near room temperature.[2] In MgO the emission is green and in CaO it is orange. We present here the first unambiguous evidence for the origin of the long-lived luminescence in MgO. The interpretation of our results leads to implications concerning the luminescence seen at low temperatures and reopens the discussion of recent models of the origin of this luminescence.[3] In the alkaline earth oxides an *F* center consists of an oxygen-ion vacany which has trapped two electrons. The main optical-absorption transition of the *F* center takes an electron from the $^1A_{1g}$ ground state to a $^1T_{1u}$ excited state. During the subsequent relaxation of the center in CaO, the electron falls nonradiatively into a $^3T_{1u}^*$ excited state from which it then decays radiatively to the ground state with a transition energy of 2.0 eV and an intrinsic lifetime of 3.3 ms.[4] Above 100 K the electron is able to escape into the conduction band by thermal excitation from the $^3T_{1u}^*$ excited state. It can then become captured by a metastable trap, which also causes a large thermoluminescence peak near 340 K. The kinetics of this process are relatively well understood in CaO, but until this present work no evidence was available concerning the nature of the traps involved.[4]

In MgO the nature of the emission from *F* centers has long been the subject of debate.[2,3,5] In this material both the *F* center and F^+ center (an oxygen-ion vacancy containing one electron) have their primary optical-absorption transition near 5 eV.[5] Excitation at this energy produces, in general, two luminescence bands, one at 3.2 eV and the other at 2.3 eV,[5,6] although it is possible to suppress either of these bands by the proper choice of crystals and parmeters under which the samples are thermochemically reduced. The intensity of the 3.2-eV band decays rapidly once the exciting light is removed and this band has been assigned to the $^2T_{1u}$-$^2A_{1g}$ transition of the F^+ center. The 2.3-eV emission band, however, is found to decay with characteristic lifetimes which range from a fraction of a second to many minutes depending on the sample and the temperature. Unlike CaO, however, cooling the sample to a low temperature does not remove the phosphorescence, so that the intrinsic lifetime of the *F* center is not known. The luminescence does not decay as a single first-order process at any temperature. Although the excitation spectrum of the 2.3-eV emission has a spectral dependence similar to the *F*-center absorption, assignment of the emission to a transition of the isolated *F* center has up to now been rejected for two main reasons. The first has been the difficulty in explaining the long-lived luminescence described above, which is the subject of this Communication. The second reason originates from preliminary theoretical calculations of the vibronic structure of the *F* center in MgO (Ref. 7) which have suggested that the electronic states may be only loosely coupled to the lattice states; i.e., the Hwang-Rhys factor has been estimated at ~4. If this were the case, vibronic structure would be expected on the 2.3-eV emission band and none has been detected so far. There are, however, some aspects of the calculations which make them quite applicable to the case of CaO but more speculative in the case of MgO.[8] In particular, the real nature of the emitting state is not yet known.

Thermoluminescence measurements clearly indicate that the lifetime of the photoluminescence at room temperature in reduced MgO and CaO is dominated by the presence of electron traps.[9] The results presented below show that these traps are mostly isolated H^- ions which are present substitutionally for O^{2-} ions. Hydrogen is a common impurity in the alkaline earth oxides and local modes at 1053, 1032, and 1024 cm^{-1} have been identified recently as due to H^- ions in MgO.[10] For the present study it was possible to demonstrate that the H^- ion is the primary electron trap responsible for the phosphorescence in MgO, since (nearly) hydrogen-free and hydrogen-rich MgO crystals have been successfully grown at Oak Ridge National Laboratory.[11] The concentration of H^- ions in MgO will be shown to cause a dramatic effect on the lifetime of the luminescence.

The crystals were grown by the arc fusion method using high-purity grade MgO powder obtained from Kanto Chemical Company, Tokyo, Japan. A large variation in hydrogen content was obtained as follows. MgO powder presoaked with water produced crystals that were cloudy, a result of the presence of cavities containing high-pressure hydrogen gas.[12] On the other hand, crystals with undetectable or bearly detectable OH^- ion concentrations could be produced when grown in a special way.[11] During the process of thermochemical reduction the crystals were heated at high temperature (2000–2400 K) and under high-pressure Mg or Ca vapor (4–7 atm) in a tantalum bomb, and then rapidly cooled. The result is the formation of oxygen-ion vacancies. H^- ions are formed when hydrogen is trapped at these vacancies.

Detailed results are presented on three representative samples labeled MgO I, MgO II, and MgO III. The concentration of F centers in these samples was estimated from the absorption coefficient at 4.95 eV. However, since the F^+ center also absorbs at this energy, we examined the relative intensity of the 3.2- and 2.3-eV emission bands to estimate the concentration of F^+ centers present. Sample II emitted only the 2.3-eV band and, therefore, contained mainly F centers. We estimate that the other samples contained between 10 and 30% F^+ centers. The concentration of F and/or F^+ centers can be estimated from the formula

$$n_F = 5.0 \times 10^{15} \alpha_F \ , \tag{1}$$

where α_F is the absorption coefficient at 4.95 eV. The coefficient in Eq. (1) is valid for both F and F^+ centers since the ratio of the half-width to the oscillator strength is comparable for both centers.[5] The concentration of H^- ions, n_H, was estimated from the absorption coefficient of the local mode at 1053 cm^{-1}, α_H, using the formula[13]

$$n_H = 3.0 \times 10^{17} \alpha_H \ .$$

A summary of the data for the three samples is given in Table I.

Luminescence was excited in the samples at 260 K with a 60-W deuterium lamp used in conjunction with a 230-nm interference filter. The emitted light was detected with an EMI 9813B photomultiplier tube and displayed on the screen of an oscilloscope and a y-t recorder. Stray light with energy above 2.7 eV was removed using a Corning CS-3-71 sharp-cut filter. Each sample was masked so that only light emitted from the same area of illuminated surface would be detected. A sample was illuminated until the emission reached a maximum intensity and then the excitation was removed. The results are presented in Fig. 1 in which the intensities at $t = 0$, $I(0)$, have been normalized. The actual values of $I(0)$ for samples I, II, and III were in the ratio 0.3:1.0:0.6, respectively.

Figure 1 clearly shows that as the concentration of H^- ions increases the luminescence at 2.3 eV becomes increasingly longer lived. None of the curves of Fig. 1 can be fitted to a single simple function, although in each case after an initial relatively rapid decay the curves correspond to a second-order process. However, if we take the period over which the intensity falls to $\frac{1}{10}$ the initial value as a reasonable measure of the phosphorescence lifetimes, then the characteristic times, τ, for samples I, II, and III are 300, 27, and 3 s, respectively. It is worth noting that the luminescence itself is not due to H^- ions since a crystal which contained H^- ions but no detectable F centers showed no 2.3-eV emission. In addition, contrary to general belief, the degree of phosphorescence does not increase with concentration of F centers as any process involving interacting pairs of F centers would require. Specifically, sample II contained about three times the concentration of F centers contained in sample I, but had a characteristic time an order of magnitude smaller.

TABLE I. Characteristics of thermochemically colored MgO samples.

Sample	α_F (cm^{-1})[a]	n_F (cm^{-3})[b]	α_H (cm^{-1})[c]	n_H (cm^{-3})[d]	τ (s)
MgO I	330	(1.6×10^{18})	11	(3.3×10^{18})	330
MgO II	820	(4.1×10^{18})	0.5	(1.5×10^{17})	27
MgO III	110	(5.5×10^{17})	0.2	(6×10^{16})	3

[a] Absorption coefficient at 4.95 eV.
[b] Calculated using Eq. (1).
[c] Absorption coefficient at 1053 cm^{-1}.
[d] Calculated using Eq. (2).

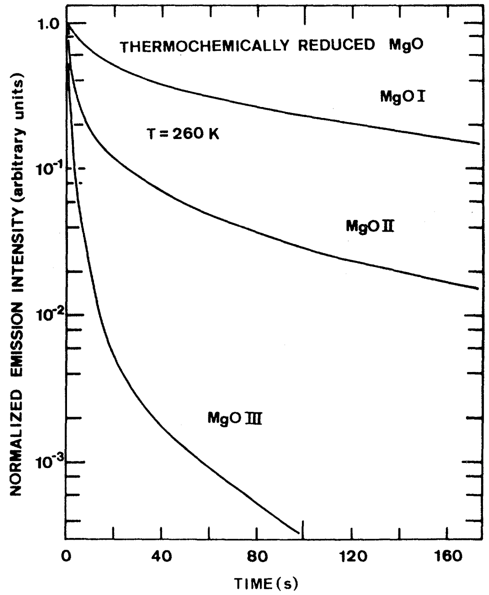

FIG. 1. Luminescence decay at 260 K of the 2.3-eV band in thermochemically reduced MgO. The concentration of H^- ions decreases from sample MgO I through MgO III (see Table I).

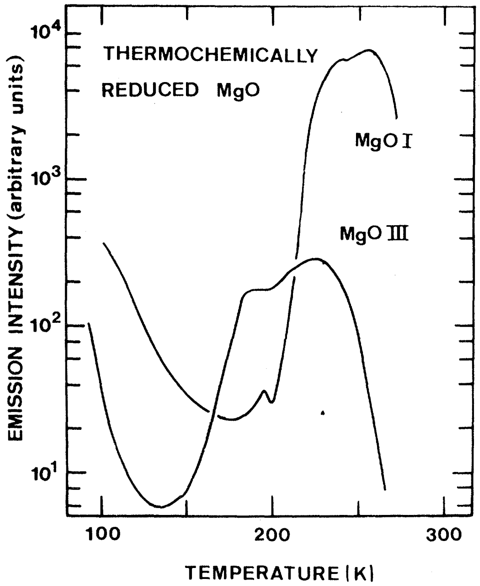

FIG. 2. Thermoluminescence curves measured from thermochemically reduced MgO. Sample MgO I contains a concentration of H^- ions about 50 times higher than sample MgO III (see Table I).

The thermoluminescence curves obtained from hydrogen-doped and hydrogen-free samples are different as is shown in Fig. 2. Notice that the intensity scale in Fig. 2 is logarithmic. For these experiments the samples were cooled to ~20 K, illuminated with ultraviolet light for a few minutes, and then heated at a rate of 5 K min^{-1}. During the large peak at 260 K the emission has a spectral dependence similar to the 2.3-eV photoluminescence band. We estimate that the thermoluminescence occurs when an electron is released from a trap with a thermal activation energy of ~0.6 eV.

H^- ions enter the lattice substitutionally for O^{2-} ions and, therefore, represent a region of net positive charge in the lattice. Our measurements indicate that the resulting electron trap causes the long-lived phosphorescence observed near room temperature and the thermoluminescence peak at 260 K. Thermoluminescence results at 2.3 eV when electrons are released from the hydrogen traps and fall back into F^+ centers. Although 0.6 eV may appear to be a small energy for thermal release of the electron from H^{2-} ions, it is worth remembering that the polarization energy associated with the surrounding O^{2-} ions is quite large and tends to reduce substantially the binding energy for electrons in oxygen-vacancy centers, e.g., the F^+ center is SrO.[14]

In summary we have demonstrated that in MgO (1) the lifetime of the 2.3-eV phosphorescence is determined primarily by the concentration of H^- ions, indicating that these ions are the long-sought electron traps responsible for the long lifetime of the *F* luminescence near room temperature; (2) H^- ions alone do not give rise to the 2.3-eV luminescence—*F* centers are required; and (3) contrary to previous belief the *F*-center concentration has no direct bearing on the lifetime of the 2.3-eV luminescence.

We speculate that the phosphorescence of the *F* center in CaO is also due to H^- ions. However, the task of demonstrating this by the method we have used for MgO is difficult since it has not proved possible yet to produce CaO without OH^- ions, or thermochemically reduced CaO without H^- ions. A similar situation also exists in thermochemically reduced sapphire where long-lived phosphorescence is observed in some samples near room temperature.[15] It is possible that H^- ions are also responsible in this case too.

One of us (R.G.) was supported during the course of this work by a grant from the Ministerio de Universidades e Investigacion, Spain. The research at ORNL was supported by the Division of Material Sciences, U.S. Department of Energy, under Contract No. W-7405-ENG-26 with Union Carbide Corporation and at Oklahoma State University by the U.S. Department of Energy under Contract No. EY-76-S-05-4837.

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[1] Commonly also referred to as "additively colored," but recent work suggests that the process is more aptly called subtractive coloration in oxides.

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