PHYSICAL REVIEW B VOLUME 30, NUMBER 4 15 AUGUST 1984

Optical properties of CaO crystals containing hydrogen

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(Received 28 November 1983)

Optical-absorption measurements show that substitutional H^- ions (that is, protons on anion sites each with two electrons) are thermally more stable than anion vacancies when thermochemically reduced CaO samples are annealed in a reducing atmosphere. Electron irradiation decreases the concentration of H^- ions and increases the concentration of oxygen vacancies with a cross section much larger than for elastic collision damage. The room-temperature lifetime of the 2.1-eV *F*-center luminescence decreases as the concentration ratio of *F* centers to H^- ions increases.

I. INTRODUCTION

It has recently been shown that high-temperature thermochemical reduction of crystals of alkaline-earth oxides introduces not only oxygen-vacancy absorption, but also sharp absorption lines in the infrared region at ~ 1000 cm^{-1}. These lines are due to local-mode oscillations of substitutional negative hydrogen ions.[1] These ions each consist of a proton surrounded by two electrons and, therefore, represent a region of local positive charge in the lattice. In thermochemically reduced MgO, electrons can be optically excited into the conduction band from *F* centers (oxygen vacancies each of which has trapped two electrons) at nearly all temperatures, and the presence of H^- ions,[2] acting as electron traps, strongly affects the optical properties of the crystals.[3,4] For example, the lifetime of the 2.3-eV *F*-center luminescence near room temperature is determined by the concentration of H^- ions present.[5] We report here on the thermal stabilities of anion vacancies and H^- ions and their effect on the optical properties of CaO crystals at room temperature. The behavior of CaO is found to be generally similar to that of MgO.

II. EXPERIMENTAL DETAILS

Substitutional H^- ions are formed during thermochemical reduction of MgO due to the presence of OH^- ions[1] and cavities[6] of high-pressure hydrogen gas, which are generally present in as-grown crystals. The source of hydrogen is adsorbed water in the starting powder. Although it is possible to minimize the concentration of hydrogen introduced into MgO crystals during growth, the hydroscopic nature of CaO makes the exclusion of hydrogen almost impossible, so that the thermochemical reduction of CaO inevitably produces crystals containing H^- ions. The CaO crystals used in the present study were grown at Oak Ridge National Laboratory using the arc-fusion method. The starting material was high-purity reagent-grade $CaCO_3$ obtained from Mallinckrodt Chemical Company. Analyses of typical starting material and the resulting crystals have been reported previously.[7,8] CaO crystals are usually cloudy because of reactions involving hydroxyl ions from $Ca(OH)_2$ present in the starting material and CO_2 evolved during fusion.[8] CaO crystals therefore contain an abundance of hydrogen. During thermochemical reduction the crystals were heated to 2100 K under 5 atm Ca vapor in a tantalum bomb, then rapidly cooled to room temperature. This process, also referred to as subtractive coloration, produces anion vacancies. Protons in the crystal can be trapped at these vacancies, forming substitutional H^- ions. The more hydrogen in the crystal the more H^- ions are formed. Thus the balance between the concentrations of H^- ions and anion vacancies depends on the concentration of hydrogen in the crystal and the details of the reduction process.

Infrared-absorption measurements were made with a Perkin-Elmer model-580 spectrophotometer. Visible- and ultraviolet-absorption measurements were made with a Perkin-Elmer model-320 spectrophotometer. *F*-center luminescence was excited in the samples with a 150-W xenon lamp used in conjunction with a Corning CS-5-58 glass filter, and detected with a thermoelectrically cooled RCA C-31034 photomultiplier tube. Electron irradiations were made with a 2.0-MeV Van de Graaff accelerator (High Voltage Engineering). During the irradiation, which lasted 1 h, the samples were wrapped in aluminum foil and cooled with flowing tap water. The temperature of the cooling water was ~ 283 K and we estimate that during irradiation the temperature of the samples increased by about 10 K. The flux of electrons on the samples was typically $\sim 15\ \mu\mathrm{A\,cm}^{-2}$.

III. RESULTS AND DISCUSSION

Defects resulting from thermochemical reduction of CaO at high temperatures are primarily anion vacancies and H^- ions. Anion vacancies are known to occur in two

TABLE I. Optical-absorption coefficients α of thermochemically reduced CaO samples (I—IV). Sample CaO V was not thermochemically reduced.

	After thermal anneal		After electron irradiation	
Sample	α_F (cm^{-1})[a]	α_H (cm^{-1})[b]	α_F (cm^{-1})[a]	α_H (cm^{-1})[b]
CaO I	2.8 (F^+)	0.5 (911)		
	~0 (F)	5.1 (880)		
CaO II	5.1 (F^+)	1.4 (911)	30.4 (F^+)	~0 (911)
	7.8 (F)	6.9 (880)	19.3 (F)	1.4 (880)
CaO V	0	0 (911)	~0	0 (911)
	0	0 (880)	~0	0 (880)
	Not thermally annealed		After electron irradiation	
Sample	α_F (cm^{-1})[a]	α_H (cm^{-1})[b]	α_F (cm^{-1})[a]	α_H (cm^{-1})[b]
CaO III	~40 (at 2.75 eV)[c]	1.8 (911)	~40 (at 2.75 eV)[c]	0 (911)
		8.8 (880)		2.3 (880)
CaO IV	42 (at 2.75 eV)[c]	1.4 (911)		
		8.3 (880)		

[a] Absorption coefficients for F^+ band measured at 3.65 eV and for F band at 3.10 eV.

[b] Absorption coefficients were measured at 911 cm^{-1} (911) and 880 cm^{-1} (880).

[c] Absorption coefficients at 3.65 and 3.10 eV were too high to be measured.

charge states: the two-electron F center and the one-electron F^+ center. The F-center absorption at 3.1 eV has been attributed to an allowed $^1A_{1g} \rightarrow {}^1T_{1u}$ transition.[9] Below ~300 K the resulting emission peaks at 2.1 eV and has been attributed to a $^3T_{1u} \rightarrow {}^1A_{1g}$ transition.[10,11] The F^+-center absorption at 3.65 eV has been assigned to a $^2A_{1g} \rightarrow {}^2T_{1u}$ transition, with a corresponding emission at 3.35 eV. The local-mode oscillations of H$^-$ ions produces two absorption bands located at 880 and 901 cm^{-1} at room temperature.[1,12,13] Based on the measurements made on several samples, Gourley and vance suggested that these two lines are intensity-correlated. However, while different samples do exhibit similar intensity ratios, measurements made on samples following electron irradiation show that this in fact is not the case. In our analysis of the results, the concentration of anion vacancies was measured from the absorption coefficients of the 3.1- and 3.65-eV bands at room temperature. Similarly, the concentration of H$^-$ ions was estimated from the absorption coefficients at 880 and 911 cm^{-1}.

Results were obtained from two pairs of samples. For each pair the individual samples were cleaved from adjacent parts of the same ingot. The first pair, samples CaO I and CaO II were used for the thermal-annealing experiments. Samples CaO III and CaO IV were not annealed. Sample CaO V was not thermochemically reduced and was used as a control. Samples CaO II, CaO III, and CaO V were subsequently electron-irradiated. A summary of the optical-absorption coefficients of both the anion-vacancy and H$^-$-ion bands at different times during the experiments described below, is given in Table I.

A. Thermal stability and radiation-induced displacement of protons

H$^-$ ions were found to be more stable than oxygen vacancies in CaO. The stability was determined by subjecting samples CaO I and CaO II to anneals of 1 h duration at 1773 K in a graphite crucible surrounded by flowing nitrogen gas. After this thermal treatment the absorption coefficients (α) at 3.65 and 3.1 eV decreased dramatically from initial values too high to measure ($\alpha \approx 200$ cm^{-1} at 3.1 eV) to less than 8 cm^{-1}. The absorption coefficients of the H$^-$ ions, however, remained unchanged. Thus, as in the case of MgO,[3] H$^-$ ions in CaO are much more stable than anion vacancies. Since the samples were in an atmosphere in which the oxygen partial pressure was very small, vacancies were probably lost by diffusing toward the sample surfaces. It has recently been shown theoretically that H$^-$ ions are very strongly bound at an anion vacancy in the surface of MgO (Ref. 14) and similar stability is expected for the bulk. No results are yet available for CaO, but similar stability for the H$^-$ ion is also expected for this material.

We now demonstrate that the infrared lines at 880 and 911 cm^{-1} are due to protons on anion-vacancy sites. Sample CaO II was electron-irradiated at room temperature after it had been annealed and therefore contained a relatively large concentration of H$^-$ ions and a relatively small concentration of oxygen vacancies (see Table I). Sample CaO III, which had not been annealed, was irradiated with an identical dose of $\sim 3 \times 10^{17}$ e/cm^2. After the irradiations, the absorption at 911 cm^{-1} vanished and that at 880 cm^{-1} had decreased for both CaO II and CaO III (see Fig. 1 and Table I). At the same time, oxygen vacancies had been created as monitored in CaO II by an increase in both the F^+- and F-center absorption bands (see Fig. 2 and Table I). The oxygen-vacancy absorption in CaO III was, however, too high to be measured accurately. These effects are aspects of the same radiation-induced process in which protons are displaced from H$^-$ sites, leaving behind oxygen vacancies. The protons then diffuse to other sites in the crystals, possibly forming new

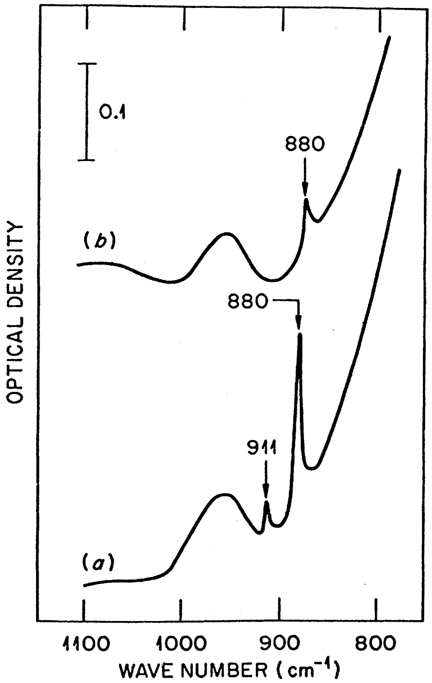

FIG. 1. Infrared spectra for H^- ions prior to irradiation (curve *a*) and after irradiation with 3.3×10^{17} *e*/cm^2 (curve *b*) for sample CaO III.

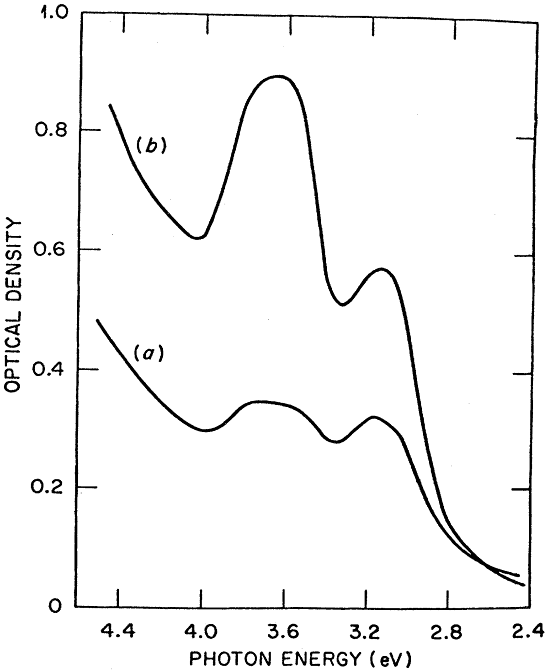

FIG. 2. Absorption spectra for oxygen-vacancy centers prior to irradiation (curve *a*) and after irradiation with 3.3×10^{17} *e*/cm^2 (curve *b*) for sample CaO II. *F* centers and F^+ centers absorb at 3.1 and 3.65 eV, respectively.

OH^- ions. The behavior of sample CaO V shows that if a sample does not contain H^- ions, electron-irradiation doses such as those used here are ineffective in producing oxygen vacancies.

It is possible to estimate the relation between the absorption coefficients at 880 and 911 cm^{-1} and the concentration of H^- ions from the results presented in Table I. In order to do this we use Smakula's equation for a Gaussian-shaped band to determine the concentrations of *F* and F^+ centers present. Taking the refractive index of CaO as 1.84, the half-widths of the *F* and F^+ bands as 0.45 and 0.32 eV, respectively, and the oscillator strength of the *F*- and F^+-center transitions as 1.0 and 0.8, respectively,[15] we obtain the following relations:

$$N_F=3\times10^{15}\alpha_F\ , \tag{1}$$

$$N_{F^+}=1.8\times10^{15}\alpha_{F^+}\ , \tag{2}$$

where *N* is the concentration of anion vacancies in units of cm^{-3}. Using these equations and the data in Table I, we estimate that the incident flux of 3×10^{17} *e*/cm^2 produced $\sim8\times10^{16}$ anion vacancies/cm^3, including both *F* and F^+ centers. If we assume that the loss of one H^- ion results in the creation of one oxygen vacancy, we can use the change in the H^--ion absorption to deduce the relation

$$N_H=1.2\times10^{16}\sum\alpha_H\ , \tag{3}$$

where N_H is the concentration of H^- ions cm^{-3} and $\sum\alpha_H$ refers to the sum of the absorption coefficients at 911 and 880 cm^{-1}.

The rapid decrease of H^--ion absorption following electron irradiation indicates that the displacement cross section for protons in CaO is comparable to that in MgO, which we have recently shown to be $\sim10^8$ b.[3] Ionizing radiation also displaces protons in other materials such as CaF_2:H. Because of the relatively open fluorite structure, however, x-ray irradiation at room temperature produces interstitial hydrogen atoms, H^0. These atoms are stable up to ~500 K, when substitutional H^- ions are formed again.[16] In KCl crystals containing hydroxyl ions, ultraviolet light splits the O—H bond, producing both interstitial H^- ions and H^0 atoms.[17] In both CaF_2 and KCl, however, x rays can produce anion vacancies (*F* centers) by anion displacement, which is not the case for CaO.

B. Lifetime of 2.1-eV luminescence

After the treatments discussed in Sec. III A, there were two pairs of samples available which had been cleaved from adjacent parts of the same ingot, and in which the concentrations of *F* centers and H^- ions were different. We were therefore able to determine the effect of different concentrations of *F* centers and H^- ions on the lifetime of the *F*-center luminescence at 2.1 eV. In these experiments the samples were illuminated at room temperature with 3.1-eV light until the 2.1-eV emission reached a maximum intensity. The light was then removed. As we have discussed previously[3] the luminescence decay which then occurs does not follow first-order kinetics. Instead, an initial relative rapid transient decay occurs, which is followed by a longer-lived second-order process. We have found that under these circumstances a convenient measure of the luminescence lifetime is the period over which the intensity falls to one-tenth of its initial value. Table II shows the luminescence lifetime for samples CaO I—CaO IV estimated in this way. The concentrations in Table II

TABLE II. Estimated oxygen-vacancy and H^--ion concentrations, and F-center luminescence lifetimes in CaO samples.

Sample	η_F (cm^{-3})[a]	η_{F^+} (cm^{-3})[b]	η_H (cm^{-3})[c]	τ_R (s)
CaO I	$<1\times10^{15}$	5×10^{15}	7×10^{16}	>800
CaO II	6×10^{16}	9×10^{16}	2×10^{16}	35
CaO III	d	d	3×10^{16}	185
CaO IV	d	d	1×10^{17}	640

[a] Calculated using the data in Table I and Eq. (1).

[b] Calculated using the data in Table I and Eq. (2).

[c] Calculated using the data in Table I and Eq. (3).

[d] Too large to be measured.

were calculated using Eqs. (1) and (3), and for samples CaO II and III are given after electron irradiation. Table II demonstrates that when the concentration of H^- ions decreases and the concentration of F centers increases, the luminescence lifetime is shortened dramatically. These results support the model that H^- ions are the traps at which electrons optically excited from F centers are temporarily trapped, as in the case of MgO. Other experiments[18] indicate that the activation energy for release of electrons from H^{2-} ions near room temperature is ~0.73 eV in CaO. The released electron can become retrapped several times at other H^- ions before being finally captured by an F^+ center, thereby giving rise to 2.1-eV luminescence. The larger the concentration of H^- ions compared to the concentration of anion vacancies, the longer the itinerant electron takes to be finally captured at an F^+ center and, hence, the longer the observed lifetime of the 2.1-eV luminescence becomes.

Although we are not concerned here primarily with the configuration of the H^- ions, one point worth noting is that the local-mode—absorption spectrum of the H^- ions consists of two intensity-uncorrelated bands. This means that not all the H^- ions are on isolated oxygen-ion sites, which have O_h symmetry. Furthermore, thermoluminescence (TL) measurements indicate that two kinds of electron traps are introduced by thermochemical reduction. These produce TL peaks at ~80 and ~320 K. The intensity of the 320-K peak is correlated with the concentration of H^- ions in the crystal. These results are consistent with a model in which H^- ions are present in two kinds of sites. For one kind the H^- ions are isolated, whereas for the other the symmetry is lowered by the presence of a nearby impurity ion (possibly a charge compensator). One possible configuration for the latter is to have an impurity on a fourth-nearest-neighbor site, i.e., the second lattice site in a $\langle 100 \rangle$ direction away from the H^- ion (the first-neighbor lattice site being occupied by a Ca^{2+} ion).[19] Although the symmetry of the resulting center would be C_{4v}, which would split the degeneracy of the local-mode oscillation, the splitting would be expected to be relatively small. The resulting spectrum could then have the observed two-band structure with one of the bands from the perturbed centers hidden under the band for the unperturbed centers. A somewhat similar situation occurs for H^- ions in mixed KCl + NaCl crystals.[20]

IV. SUMMARY

First, we have shown that in CaO as in MgO, H^- ions are thermally more stable than anion vacancies. Whereas anion vacancies are substantially annealed in a reducing atmosphere at 1723 K, H^- ions can survive without loss. Second, electron irradiation reduces the absorbance of H^- ions and increases the absorbance of anion vacancies, demonstrating that the infrared lines are due to protons located at oxygen-vacancy sites. Third, the lifetime of the 2.1-eV luminescence decreases when the concentration ratio of H^- ions to F centers decreases, showing that H^- ions serve as electron traps and thereby determine the luminescence lifetime.

ACKNOWLEDGMENTS

We are indebted to M. M. Abraham and M. Mostoller for helpful discussions about this work. The research at Oak Ridge National Laboratory was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. W-7405-eng-26 with the Union Carbide Corporation.

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