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PROSPECTS FOR WAVELENGTH TUNABLE LASERS BASED ON VACANCY DEFECTS IN ALKALINE-EARTH OXIDES

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PROSPECTS FOR WAVELENGTH TUNABLE LASERS BASED ON VACANCY DEFECTS IN ALKALINE-EARTH OXIDES*

1. INTRODUCTION

Research on color centers in the alkali halides has proven fruitful in that the recent development of tunable lasers was a direct outgrowth of the studies.[1,2] It is expected that research on the alkaline-earth oxides will also bear fruit in this area. In this article we discuss the merits and problems of using defects for tunable lasers. Our discussions shall be confined to CaO and MgO crystals.

Vacancies such as the F^+ center (an anion vacancy with one electron which is therefore positively charged with respect to the lattice) constitute a four-level system. Vacancies can provide higher gain than transition metal or rare-earth ions. The equation for the gain coefficient α is

$$\alpha = \sigma N^* = \frac{\lambda_o^2 \eta}{8\pi n^2 (\Delta\upsilon)\tau} N^* \qquad (1)$$

where σ is the cross section, η the quantum efficiency, λ_o the peak wavelength of the band, $\Delta\upsilon$ the full-width-at-half-maximum of the band, τ the luminescence decay lifetime and N^* the excited-state population. The cross section for vacancies are typically $\sim 10^{-17}$ cm^2 and for transition metal ions $\sim 10^{-20}$ cm^2. This difference is largely due to the luminescence decay time, which is $\sim 10^{-8}$ s for vacancies but several orders of magnitude larger for certain impurities.

2. METHODS FOR DEFECT PRODUCTION

As in the alkali halides, the two methods for producing anion vacancies in the oxides are either by irradiation with energetic particles or by thermochemical reduction (also known as additive coloration, subtractive coloration, or electrolytic coloration).[3] However, the conditions under which sufficient vacancies are produced are much more stringent for the oxides. For example, the electron dose required to produce 10^{17} anion vacancies/cm^3 in MgO and CaO is about 10^6 greater than that required to produce a similar concentration in the alkali halides. This magnitude requires long hours of irradiation with a van de Graaff generator. Neutron irradiations are simpler since large concentrations of defects can be produced readily. Furthermore, one need not be concerned with the stopping power for neutrons as for electrons: the range of neutrons can be considered as infinite, whereas for 2 MeV electrons it is a few millimeters. For thermochemical reduction (TCR), the temperature and pressure requirements (of the cation metallic vapor) are likewise much more demanding. Typically for

MgO and CaO, temperatures of 2000–2300 K and pressures of 4 to 7 atmospheres of Mg and Ca vapor, respectively, are required to produce anion vacancies.

3. ANION VACANCIES AND THERMOCHEMICAL REDUCTION

In the alkaline-earth oxides, TCR produces anion vacancies whose optical properties are more suited for tunable lasers than those produced by neutron irradiations. There are several advantages for TCR: First, anion vacancies produced by neutrons do not survive temperatures much above room temperature.[4] The reason is that interstitials are also created during irradiation, and being much more mobile than vacancies, they readily recombine with the vacancies. However, if there are no interstitials, as in TCR crystals, the vacancies can survive temperatures up to 1100 K. Second, TCR suppresses the formation of trapped-hole centers (V-type centers), which are a consequence of photoconversion. Photo-excitation or ionizing radiation can produce holes, which can be trapped at adjacent O^{2-} ions, forming O^- ions, by existing cation vacancies compensated by impurities such as Al^{3+}, H^+, and F^- ions. They are referred to as V_{Al}, V_{OH}, and V_F centers respectively.[5] The optical absorption bands for these centers are very broad, typically with a FWHM of 1.1 eV, and cover most of the visible spectrum in MgO and CaO. The absorption peaks are at 540 nm (2.3 eV) and 670 nm (1.85 eV), respectively. Since the F^+ and F centers luminesce in the visible and near-visible region in both hosts (Table 1), the presence of trapped-hole centers quenches the luminescence. In TCR crystals anion vacancies are created nonstoichiometrically. The mass-action law dictates that as anion vacancies are created, cation vacancies are subdued.[6] The third advantage of TCR is the quantum efficiency of the luminescence. Figure 1 illustrates the luminescence intensity of the F^+ center in a neutron-irradiated and a thermochemically reduced MgO measured under identical conditions. The optical density in both samples was greater than unity. The luminescence intensity of the TCR sample was a factor of 15 more intense.

Table 1. Optical absorption and luminescence peaks of the F^+ and F centers in CaO and MgO crystals.

	F band		F^+ band	
	Absorption	Emission	Absorption	Emission
CaO	400 nm (3.1 eV)	605 nm (2.05 eV)	340 nm (3.65 eV)	370 nm (3.35 eV)
MgO	247 nm (5.0 eV)	515 nm (2.4 eV)	252 nm (4.92 eV)	380 nm (3.26 eV)

However, there are also problems for TCR; specifically, crystal darkening and long-lived phosphorescence. In the first case, the strong reducing atmosphere causes a crystal darkening effect which is strongly sample dependent.

Transmission electron microscopy studies in MgO revealed the presence of Fe and Fe-Cr precipitates.[7] These precipitates causes Mie scattering which affects a broad spectrum covering the entire visible region.

The second problem associated with TCR is the F-center phosphorescence. It is generally known that the F-center luminescence lifetime in thermo-chemically reduced CaO and MgO is strongly sample dependent and can last for more than 10^3 s.[8,9] We identified the cause of the phosphorescence as hydride (H^-) ions. To a greater or lesser extent, all oxide crystals contain protons. During TCR oxygen vacancies are formed, which in their natural state are neutral

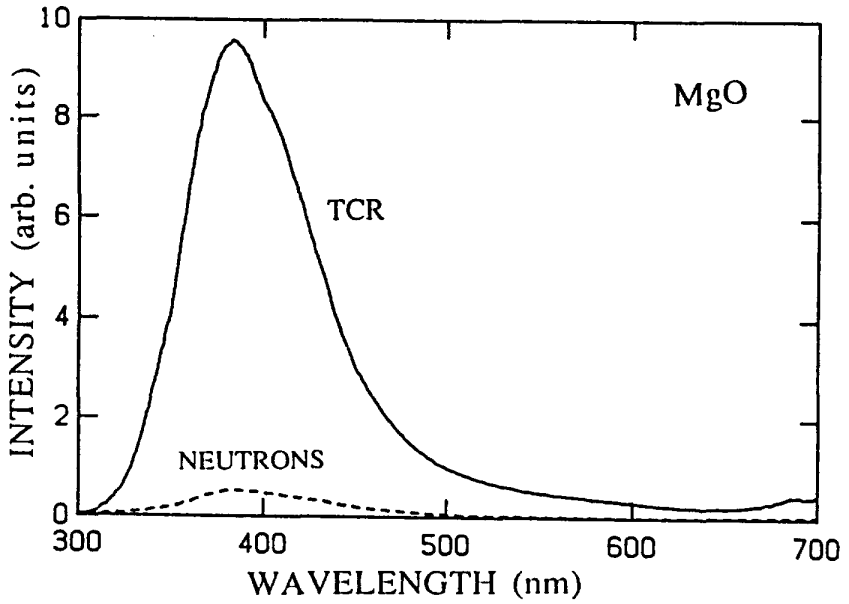

Fig. 1. Luminescence intensity of the F^+ center vs. wavelength for TCR and a neutron-irradiated MgO crystal. The experimental conditions were identical.

2-electron F centers. Protons in the crystals are highly mobile at elevated temperatures and can occupy some of the vacancies to form H^- or perturbed H^- ions (to be referred to simply as H^- ions). They can be identified by vibrational modes[3] which absorb near 1000 cm^{-1}. The H^- ion is a proton with two electrons substituting for an O^{2-} ion, and is, therefore, positively charged with respect to the lattice. F centers and H^- ions normally co-exist in a TCR crystal. During optical pumping of the F band in MgO, an electron from the $^1A_{1g}$ ground state is excited to a diffuse $^1T_{1u}$ state (5.0 eV), which lies <0.01 eV below the conduction band.[10] The electron is therefore thermally stimulated into the conduction band, from which it can be trapped by an H^- ion, thus forming an H^{2-} ion and leaving behind a F^+ center (see Fig. 2). Even though the H^{2-} ion is electrically neutral with respect to the lattice, it is metastable near room temperature by virtue of the presence of the three electrons, the outermost of which can be thermally excited into the conduction band (CB). There, it can either return to a positively charged F^+ center, resulting in F emission (2.4 eV), or be captured by another positively

charged H^- ion, thereby further delaying the inevitable return to the F^+ center. It is this successive capture by H^- ions that leads to the long phosphorescence

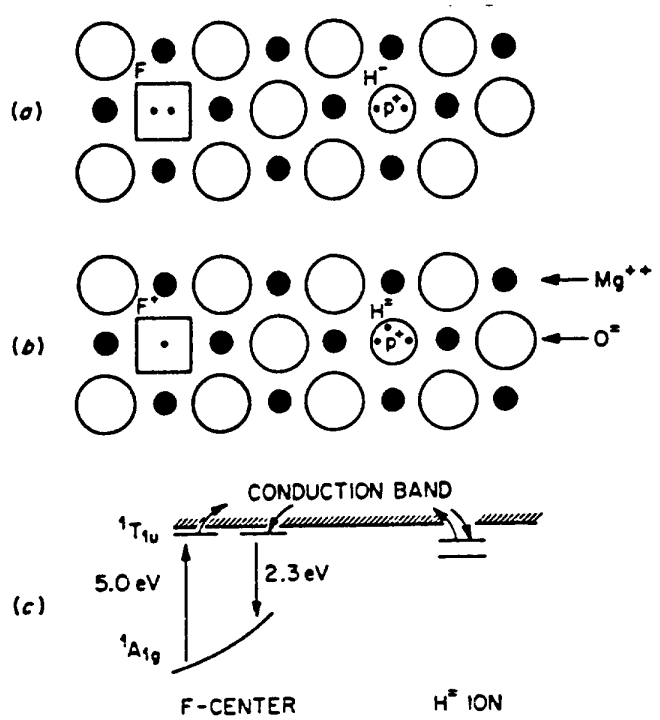

Fig. 2. Schematic MgO lattice containing F centers and H^- ions (a) before and (b) during excitation. (c) Energy-level diagram for the F center and H^{2-} ion.

lifetime. A relatively high H^- concentration implies a high probability for successive capture by H^- ions, resulting in a long-lived luminescence.

The situation in CaO:Ca is somewhat similar (Fig. 3). F centers absorb at 3.1 eV due to a $^1A_{1g} \rightarrow {}^1T_{1u}$ transition, followed by relaxation to a $^3T_{1u}$ excited state. At low temperatures, a radiative $^3T_{1u} \rightarrow {}^1T_{1u}$ transition occurs, producing F luminescence at 2.1 eV.[11-13] Above 100 K the electrons from the excited F centers are released to the conduction band via a thermally assisted process with an activation energy of ~0.1 eV. The electron is then captured by a H^- ion to form a H^{2-} ion. The H^{2-} ion lies 0.73 eV below the CB edge[8] and is responsible for the F phosphorescence in a manner similar to that in MgO. Upon excitation with 2.5 eV light at either 300 or 77 K, F luminescence is readily given off. This indicates that the excited states of the H^{2-} ions are very close to the CB, probably within 0.01 eV.

4. HYDRIDE IONS AND THE CHARGE STATE OF OXYGEN VACANCIES

The absorption and emission bands of the F^+ and F bands in CaO and MgO are known and are given in Table 1. It is noted that although the absorption bands of the F^+ and F centers occur at different wavelengths in CaO, they coincide at 4.95 eV (250 nm) in MgO.[14]

It is clear that H^- ions are the cause of the long-lived F phosphorescence in CaO and MgO. Therefore, it is pertinent to examine how the absence of protons affect the luminescence lifetime and other optical properties of anion vacancies. Protons can be removed either before or during thermochemical reduction, albeit not easily. The loss of protons results in a low H^- concentration and the production of anion vacancies which are primarily in the F^+ charge state in both CaO and MgO. The absorption bands of oxygen vacancies produced in crystals of

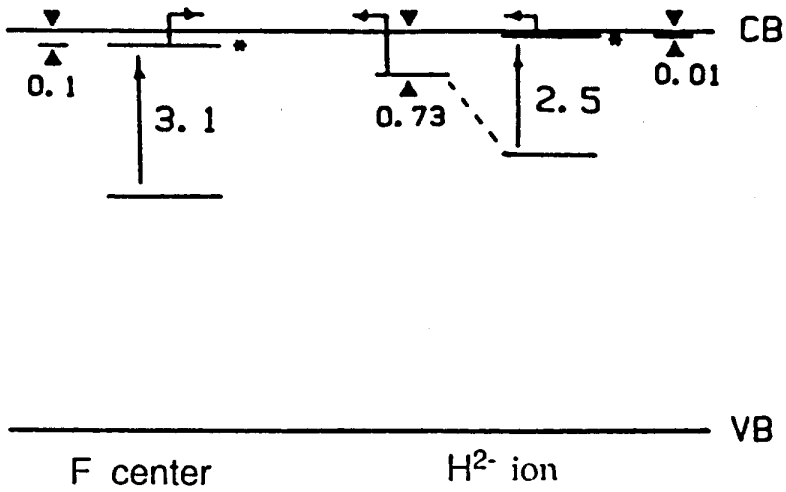

Fig. 3. Energy level diagram of F center and H^{2-} ions in CaO:Ca:H.

low and high hydrogen content are illustrated for CaO in Fig. 4. TCR crystals containing hydride ions, referred to as CaO:Ca:H, clearly favor the two-electron F center, whereas those with low hydride concentration, referred to as CaO:Ca, favor the F^+ center. The absorption coefficients were ~120 and 12 cm^{-1} respectively, corresponding to concentrations of 1×10^{18} and 1×10^{17} cm^{-3}.

Exciting the F band in the CaO:Ca:H crystal with 400 nm light results in the long-lived phosphorescence which peaks at 630 nm, shown on the right of Fig. 5. Exciting the F^+ band in the CaO:Ca crystal with 330 nm light, an emission at 375 nm is obtained (Fig. 5, left). The F^+ absorption and emission spectra are similar to those obtained in neutron-irradiated CaO crystals and confirm that we have an F^+ band in CaO:Ca crystals. The lifetime of the F^+ luminescence is many orders of magnitude shorter than that of the F luminescence, although it still exhibits components in the 10 ms range.

5. PHOTOCONVERSION

The excited states of the F center in both MgO and CaO are sufficiently close to the CB that photoconversion is inevitable, as evidenced by the trapping of electrons by hydride ions. Therefore, the F center is not a viable candidate for tunable lasers. On the other hand, photoconversion for the F^+ center is less

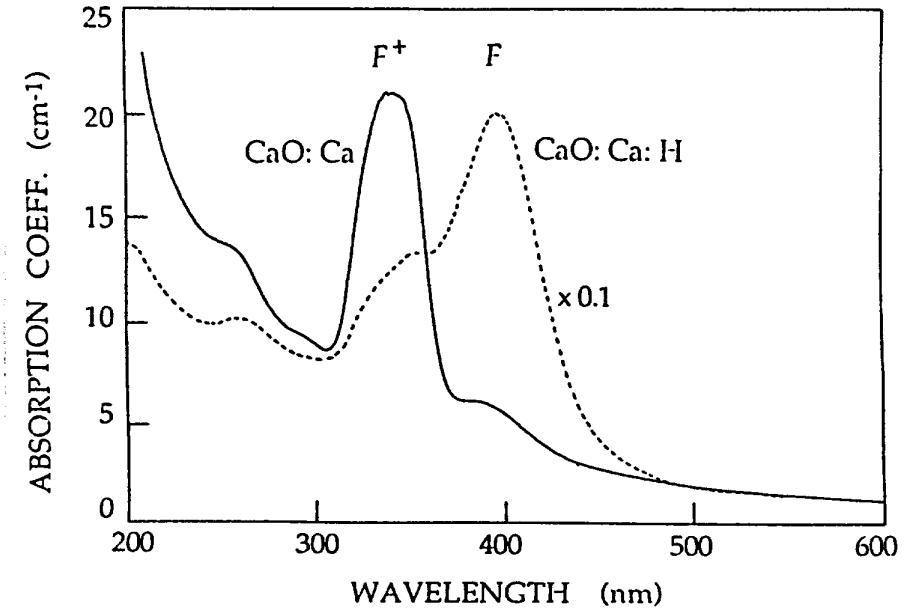

Fig. 4. Optical absorption spectra of CaO: Ca and CaO: Ca: H crystals.

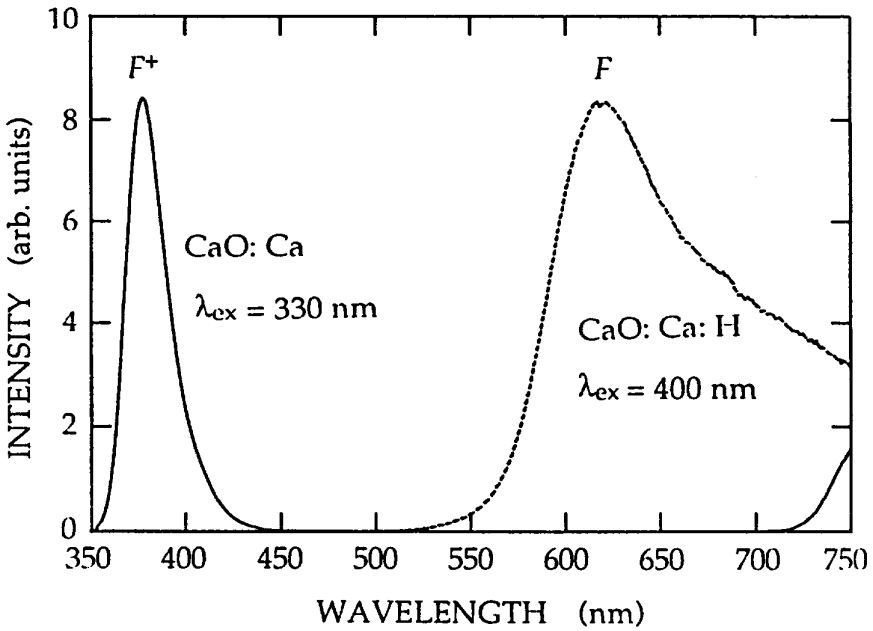

Fig. 5. Emission spectra of CaO: Ca and CaO: Ca: H excited at 330 and 400 nm respectively.

obvious. After all, in a positively charged environment, the electronic wave function of the F^+ center is expected to be much less diffuse. However, in both MgO and CaO, there is strong evidence for photoconversion during optical pumping of the F^+ center. First, trapped-hole centers are formed.[6] When the electron from the F^+ center is in an excited state, the strong polarization demands an electron from a nearby O^{2-} ion, leaving behind a hole. The hole migrates and is trapped by a Mg- or Ca-vacancy charged-compensated by an impurity, as discussed in Section 3. Second, in CaO the F absorption band is in the region of the F^+ fluorescence. In effect, exciting the F^+ band is tantamount to exciting the F band simultaneously. An electron from the F center is presumably released into

the CB and can be trapped by defects. Third, recent time-resolved studies of luminescence spectra from F and F^+ centers in MgO suggests that the F^+ first-excited state lies close to the CB edge.[15]

5. CONCLUSIONS

The problems of hydride ions and Mie scattering from second phases in TCR crystals can be resolved. However, the most serious problem encountered in attempting to use anion vacancies as a laser-active color center is of an intrinsic nature: photoconversion. It is independent of the method of defect production, whether by TCR or neutron irradiation. Therefore, to avoid this problem it is necessary to find a way to localize the electronic wave functions at the defect. One possibility is to introduce a perturbing defect.

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