Hydrogen Plasma Treated Calcium Fluoride

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Ionizing radiation is not very effective in producing color centers in pure CaF_2 because of the existence of Frenkel pairs. To produce color centers, CaF_2 either has to be doped with oxygen, manganese, etc., or subjected to a high electric field during X-ray irradiation. In this work, we have succeeded in producing color centers in pure CaF_2 by subjecting it to hydrogen plasma. CaF_2 reduced by hydrogen plasma shows absorption at 375, 515, and 560 nm corresponding to F, M, and colloidal Ca centers, respectively. The hydrogen plasma also introduces hydride ions in the lattice sites, giving rise to an IR absorption band at 956 cm^{-1}. The hydrogen plasma treated CaF_2 also shows an increase both in hardness and in crystallinity.

Introduction

Very little is known about the optical properties of superionics like calcium fluoride when exposed to hydrogen plasma.

Color centers in calcium fluoride (CaF_2) crystals have been studied extensively ever since the pioneering work of Mollwo,[1] who colored CaF_2 both electrolytically and additively. Optical absorptions are obtained at 375 (α band or F band) and at 525 nm (β band or F_2 band).[2,3] Ionizing radiation is ineffective in forming color centers in pure CaF_2. This is explained as being due to the existence of negative ion vacancies as Frenkel pairs (an interstitial negative ion associated with the vacancy it has created). However, F centers can be produced in CaF_2 at room temperature by X-ray irradiation if CaF_2 is doped with oxygen, manganese, etc. More recently, F centers have been produced in BaF_2 by quenching the crystal from a temperature of 700 °C and later irradiating with X-rays.[4] Similarly, color centers have been produced in CaF_2 by either X-irradiation under high electric field or γ-irradiation.[2,5] De and Rao[2,5] observed two prominent absorption bands, one at 375 nm corresponding to an F center and the second at 580 nm corresponding to a colloidal calcium band. Neither X-irradiation, even for prolonged times of a few hours, nor heating in H_2 at 900 °C produces any color in pure CaF_2. However, room-temperature X-irradiation of CaF_2 preheated in hydrogen at 900 °C leaves the CaF_2 crystal with interstitial hydrogen atoms[6] and gives rise to strong optical absorption bands associated with electron excess centers.[7]

Hydrogen plasma provides a convenient way of producing, apart from hydrogen molecules, excited hydrogen atoms and high-energy radiation simultaneously. CaF_2, subjected to hydrogen plasma, should, therefore, manifest color centers and associated properties. The present work reports data on the effect of hydrogen plasma on the optical, structural, and mechanical properties of CaF_2.

Experimental Procedure

Single-crystal CaF_2 cut along the (111) plane was obtained from Ceres Corp. Optical studies were carried out using a Perkin-Elmer Lambda 5 UV–vis spectrophotometer for the UV–visible region and a Nicolet 7000 Fourier transform spectrophotometer for the IR region.

A Phillips diffractometer, Model ADP 3600, was used both to obtain crystallographic data and to irradiate CaF_2 with X-rays.

Vicker's hardness measurements, using a Leco Tester, and a diamond indentor with a 1000-g load were made on an average of five widely spread indentations. All measurements were made at room temperature.

Hydrogen plasma treatment of CaF_2 single crystals was carried out using a microwave plasma chemical vapor deposition system similar to the one described by Kamo et al.[8] The system consists of microwave (2.45 GHz) generating equipment, a reaction chamber, and a gas flow and pressure control system. A single crystal of CaF_2 on a boron nitride holder was placed in a fused quartz tube, which was inserted into a rectangular waveguide

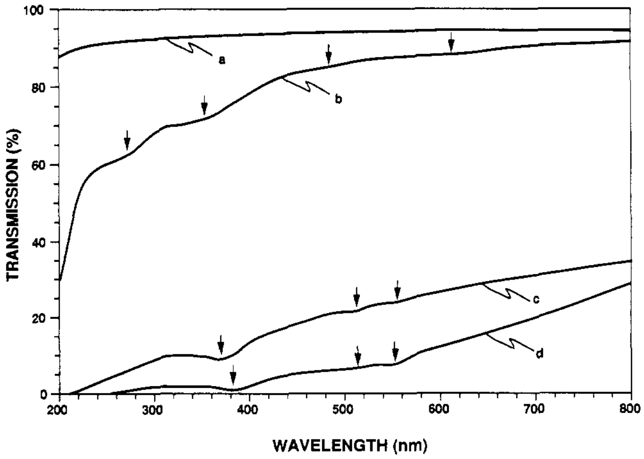

Figure 1. Hydrogen plasma induced absorption centers in the UV–visible region: (a) pure untreated CaF_2; (b) CaF_2 plasma treated for 10 min (250 W); (c) CaF_2 plasma treated for 20 min (370 W); (d) CaF_2 plasma treated for 10 min (460 W).

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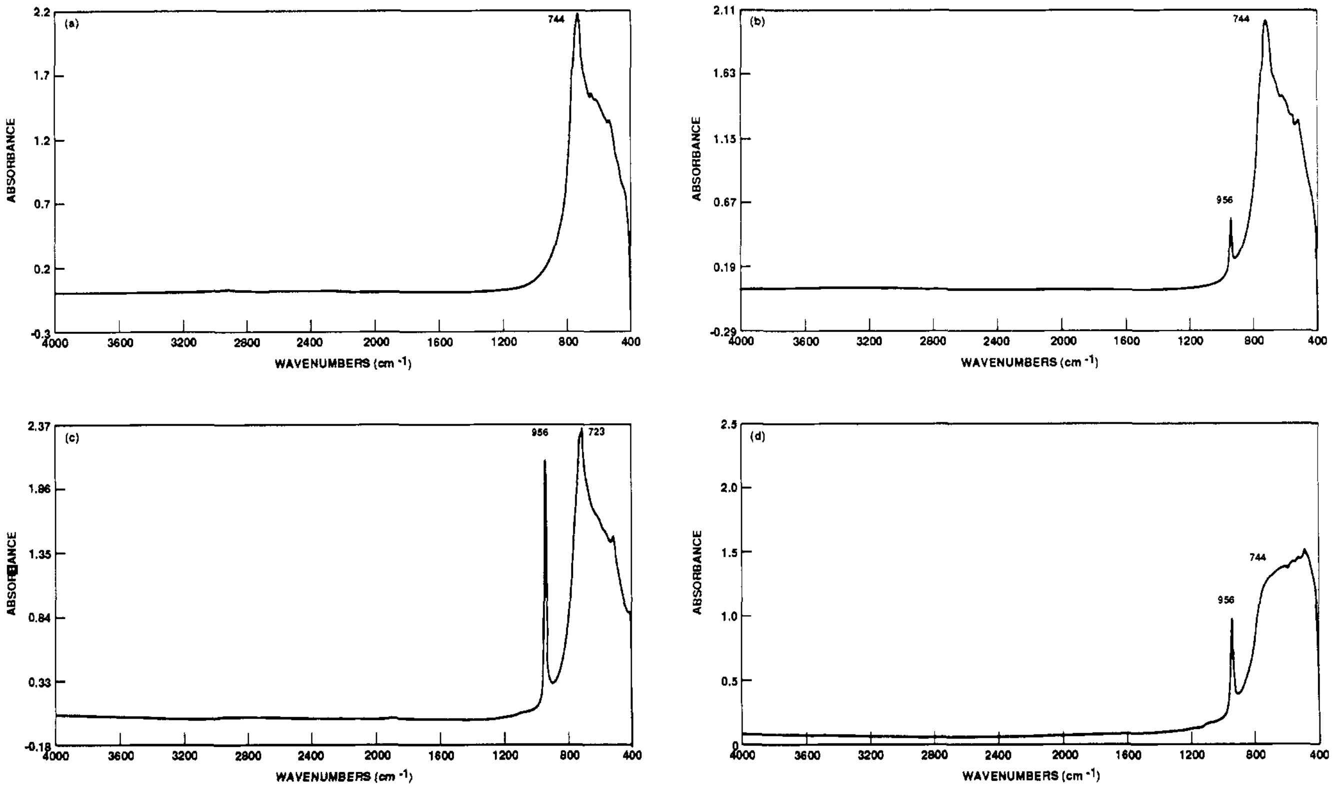

Figure 2. Hydrogen plasma induced absorption centers in the IR region: (a) pure untreated CaF_2; (b) CaF_2 plasma treated for 10 min (250 W); (c) CaF_2 plasma treated for 20 min (370 W); (d) CaF_2 plasma treated for 10 min (460 W).

perpendicularly. Microwaves generated by a magnetron were guided through an isolator, a power monitor, and a three-stub tuner to the fused quartz tube producing a plasma around the crystal. A hydrogen gas flow rate of 100 SCCM and a pressure of 60 Torr were employed. The microwave power and the time of exposure of the CaF_2 crystal to the plasma could be varied.

Results and Discussion

Optical Studies. Optical absorption measurements of hydrogen plasma treated CaF_2 reveals the presence of color centers in the region 200–800 nm. The characteristic wavelength and intensity of the absorbing centers depend not only on the duration of the plasma treatment, but also on the microwave power producing the plasma. Thus, when a single crystal of CaF_2 is exposed for 10 min to hydrogen plasma generated with 250-W microwave power, the crystal turns grey and absorbs strongly at 270 and 375 nm, and very weakly at 480 and 600 nm (Figure 1b). In the IR region, a sharp absorption band appears at 956 cm^{-1} (Figure 2b). On further exposure to the hydrogen plasma for another 20 min at 370 W, the bands at 270, 480, and 600 nm disappear, the band at 375 nm grows in intensity, and new bands appear at 515 and 560 nm (Figure 1c). In the IR region, the band at 956 cm^{-1} grows rapidly, accompanied by weak absorptions at 1100, 1950, and 2920 cm^{-1} (Figure 2c). A CaF_2 crystal exposed for 10 min to hydrogen plasma generated with a microwave power of 460 W turns pinkish-yellow and fractures due to strain. The strain leads to the broadening of the IR bands (compare Figure 2d with 2a, 2b, and 2c). The UV–visible region shows two strong absorption bands at 380 and 560 nm and a weak band at 520 nm (Figure 1d). In the IR region, a strong, sharp band appears at 956 cm^{-1} accompanied by very weak absorption bands at 1100, 1950, and 2920 cm^{-1} (Figure 2d).

In the UV–visible region, the bands at 375, 515, and 560 nm can be identified as F, M, and colloidal Ca centers, respectively.[4,5,9] The F center in calcium fluoride is one electron in an anion vacancy. Absorptions at around 270, 480, and 600 nm have been reported by Smakula[10] and Bontinck.[11] Although the bands at 480 and 600 nm are very weak and perhaps could be attributed to impurities,[9] the band at 270 nm is strong. In analogy with alkali-metal halides, one is tempted to attribute it to a U_2 center, which is an interstitial hydrogen atom.[1,2] Heating CaF_2 in hydrogen at 800 °C, followed by X-ray irradiation, results in incorporation of H atoms in interstitial positions[6] as well as in H– ions in F– sites.[7] Hydrogen plasma provides not only H atoms but high-energy ionizing radiation as well. H atoms enter the CaF_2 crystal and occupy interstitial positions, giving rise to U_2 centers. The plasma also introduces H^- ions in the lattice sites, giving rise to the IR band at 956 cm^{-1}, the fundamental vibration mode of H^- in CaF_2 crystal.[7] On further exposure to the H_2 plasma, the U_2 center gets converted to F centers[12] (e.g., the 270-nm band disappears and the 380-nm band grows). H^- ions on the lattice sites also increase in concentration, and, hence, the 956-cm^{-1} band grows, accompanied by second and third harmonics at 1950 and 2920 cm^{-1}. The appearance of the new bands at 515 and 560 nm suggests only that F centers are coagulating to form M and colloidal calcium centers.

In short, hydrogen plasma produces the following absorption centers in CaF_2: U_2 center (H atom at an interstitial position) + F center (one electron in an anion vacancy) + H^- ion at an F^- lattice site, which on further plasma exposure results in the growth of an F center, partial coagulation of F centers to form M and colloidal Ca bands, and the growth of the H^- ions at the F^- lattice sites.

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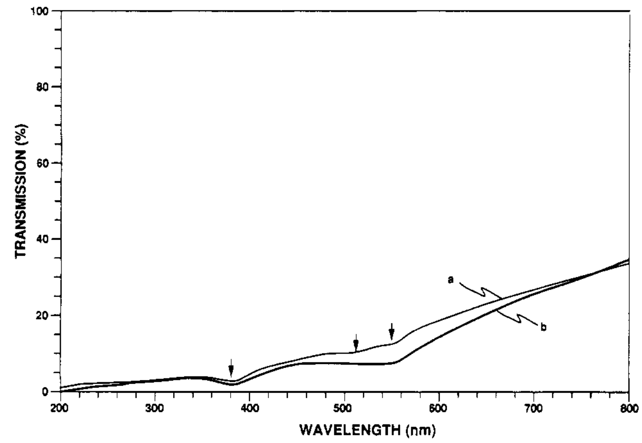

Figure 3. Effect of X-irradiation on the absorption centers in hydrogen plasma treated CaF_2: (a) plasma treated for 10 min (460 W); (b) sample (a) X-irradiated for 50 min.

Table I. Effect of Plasma Treatment and X-irradiation on Vicker's Hardness of CaF_2

sample treatment	hardness, kg/mm^2
untreated CaF_2	176
CaF_2 subjected for 10 min to plasma (460 W)	249
sample (b) exposed to X-rays for 2 h	183

When the plasma-reduced CaF_2 was subjected to 2-h of X-ray irradiation, the pinkish-yellow crystal turned dark pink. The optical absorption reveals that the absorption band at 380 nm remains unchanged, at 520 nm it disappears, and at 560 nm it doubles in intensity, i.e., the band at 560 nm grows at the expense of the band at 520 nm (Figure 3).

X-ray Diffraction Studies. Both untreated and the hydrogen plasma treated CaF_2 (cut along the 111 axis) exhibit diffraction at d = 3.155 Å (2θ = 28.25°) in agreement with the literature value[16] (Figure 4). However, the diffraction peak in reduced CaF_2 has grown in intensity (and its half-width is reduced); the peak is sharper, suggesting higher crystallinity in that orientation, e.g., reduction in the concentration of stacking faults and/or dislocations.

Hardness Studies. The Vicker's hardness of CaF_2 has been studied by O'Neill et al.,[13] who showed anisotropy in hardness on the (001) and (111) planes. Our CaF_2 crystal was cut slightly off the (111) plane, and our average Vicker's hardness for unreduced CaF_2 was 176 kg/mm^2, which is in fair agreement with the value of 165 kg/mm^2 found by O'Neill et al.[13] The plasma-treated crsytal showed a value of 249 kg/mm^2 for the Vicker's hardness (Table I). The increase in hardness can also be understood in terms of the increase in crystallinity in the (111) plane. Point defect complexes and γ-irradiation have been shown to increase the hardness of CaF_2.[14,15]

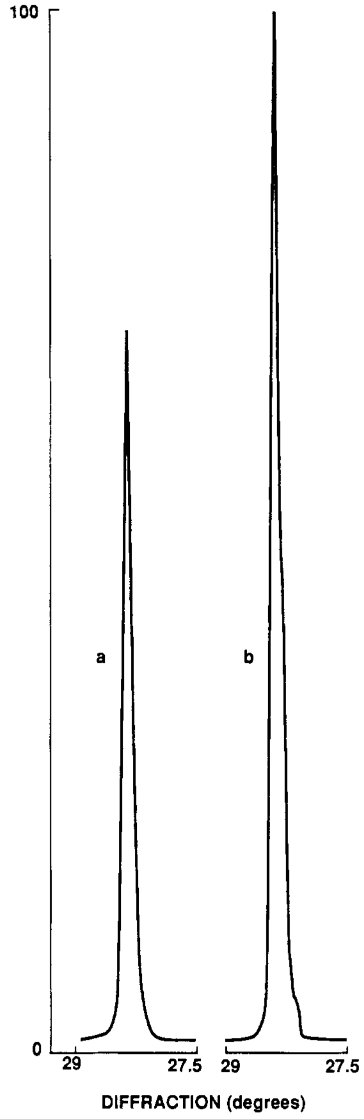

Figure 4. Effect of hydrogen plasma treatment of CaF_2 on the intensity of the X-ray diffraction peak at 2θ = 28.25° (X-ray diffractometer's full-scale range set at 3000 counts per second: (a) pure untreated CaF_2; (b) CaF_2 plasma treated for 10 min (460 W).

As described earlier in the section on Optical Studies, irradiation with X-rays of the plasma-reduced CaF_2 resulted in eliminating the absorption at 520 nm and enhancing the 560-nm absorption corresponding to the colloidal Ca. This treatment (X-ray irradiation following plasma treatment) also influenced the hardness of CaF_2, i.e., the Vicker's hardness dropped from 249 kg/mm^2 before X-ray irradiation to 183 kg/mm^2 after the irradiation (Table I). This change suggests that the increase in the concentration of colloidal Ca softened CaF_2.

Registry No. CaF_2, 7789-75-5; H_2, 1333-74-0.

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