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Optical absorption and luminescence of 14-MeV neutron-irradiated CaF_2 single crystals

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Abstract

The effects of 14-MeV neutron irradiation (1.1×10^{19} n/m^2) on crystalline CaF_2 have been examined by optical absorption and luminescence techniques to evaluate its suitability as a window material for fusion energy applications. For comparison, similar studies were done on unirradiated and X-irradiated samples. It is confirmed that pristine CaF_2 exhibits excellent optical transmission in the spectral region 200–1000 nm. X and neutron irradiation induce similar optical absorption spectra with maximum absorption coefficients approximately 1.6 and 0.8 cm^{-1}, respectively. Thermally stimulated luminescence glow curves are induced by X-ray (11.55 kGy) and neutron exposures; peaks occur at 423, 534, 596 and 479, 550, 605 K, respectively. Thermal annealing experiments show that the major absorption peaks decay in concert with appearance of the first glow peak, which is attributed to an electron trap. Thus, the major absorption bands are associated with F and F-aggregate centers. The relative ease with which these centers are produced strongly suggests that CaF_2 is not a good final optic window material for fusion energy applications.

PACS: 76.30.Mi; 78.50.−w; 78m.60.Kn; 61.80.Hg

1. Introduction

High-purity crystalline CaF_2 is an excellent optical window material because of its high transmissivity over a broad spectral range and its resistance to attack by most acids and bases. However, when subjected to X, γ or neutron irradiation it suffers enhanced optical absorption in the ultraviolet (uv) and visible portions of the electromagnetic spectrum due to the formation of radiation-induced color centers [1]. Nevertheless, there is much current interest in crystalline CaF_2 due to its use in deep uv lithography and its possible application as a final optic window in inertial fusion energy experiments. In the latter application a driver beam initiates implosion of encapsulated deuterium and tritium with the release of fusion energy accompanied by 14-MeV neutrons, X-rays and debris ions [2]. The utility of CaF_2 as a final optic window material will primarily be determined by the extent of radiation damage induced by these fusion reaction products. In the present work we examine the effects of 14-MeV neutron irradiation on crystalline CaF_2.

Previous research on CaF_2 mainly has been concerned with color centers induced by X and γ radiation or by additive coloration in pure and lanthanide-doped specimens. The identification of F centers and their aggregates (M and R centers), along with self-trapped holes (V_k centers) and self-trapped excitons, has primarily resulted from optical absorption, luminescence, and electron spin resonance studies. These results have been summarized in the excellent book by Hayes [3].

In contrast, very little work on neutron-irradiated CaF_2 has been presented in the literature. Bontinck

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investigated the optical absorption induced in CaF_2 by reactor neutrons at pile temperature and compared the results to X-ray-induced absorption [4]. Kamikawa and Ozawa examined the effects of reactor neutron irradiation on color center formation in CaF_2 at liquid nitrogen temperature and found an absorption spectrum similar to the pile-temperature irradiated one [5]. A noted difference in the two spectra was the presence of a band near 580 nm in the low-temperature irradiated sample. Thermally stimulated luminescence (TSL) and F-center annealing in CaF_2 following reactor neutron irradiation at 20 K has been reported by Atobe [6]. The main result of this work was demonstration that TSL glow curves are related to the thermal annealing of F centers and that these centers play an important role as recombination sites in the TSL process.

To our knowledge, the effect of 14-MeV neutron irradiation on crystalline CaF_2 has not been discussed in the literature. Therefore, the objective of the present paper is to utilize luminescence and optical absorption techniques to characterize as-received and 14-MeV neutron-irradiated CaF_2. Comparison of the results will provide important information on the radiation sensitivity of this material and its worthiness as a final optic window material in inertial and magnetic fusion energy applications.

2. Experimental aspects

2.1. Samples and irradiation facility

High-purity, single-crystal CaF_2 samples of 10.0×10.0 mm^2 and 2.2-mm thickness were obtained from Saint-Gobain Crystals and Detectors. The highly polished samples were used in the as received condition for all experiments.

14-MeV neutron irradiation was provided by a commercial deuterium–tritium generator typically operating at 3.0 mA beam current and 160 kV. The ion source produced about 90% molecular ions, however, so the effective beam energy was reduced to approximately 80 keV. Thus the angular distribution of neutron energy was 14.68 MeV at 0°, 14.06 MeV at 90°, and 13.47 MeV at 180°. Since the samples were placed in the forward beam direction, the neutron energy utilized in the present experiment was 14.68 MeV.

Neutron fluence was measured by an Al activation foil placed directly behind the CaF_2 samples, and by Al and Fe activation foils placed at the neutron generator collimator exit slit. Gamma rays from the activated foils were counted and used to derive the neutron generator output, which was 3.0×10^{10} n/s when operated at 3.0 mA beam current and 160 kV. The total neutron fluence received by the CaF_2 samples was 1.1×10^{19} n/m^2. Neutron flux at the sample could not be quantified as a single number because the specimens were irradiated in 55 separate but unequal intervals (total exposure time of 171.4 h) during a two and one-half month period. Initial exposures were done with a beam current of 2.5 mA at 150 kV, and the final exposures were done with 3.0 mA beam current at 160 kV. The normalized (3.0 mA, 160 kV) exposure time, accounting for periods of reduced intensity, was 130.0 h. An approximate estimate of the displacement damage dose and ionizing radiation dose from neutron exposure is 2 and 70 kGy, respectively [7].

X-irradiation was provided by a Mo-target X-ray tube operating at 50 kV and 40 mA with an effective energy of approximately 25 keV. The measured dose rate at the sample position was 1.75 Gy/s (in air).

2.2. Optical absorption

Optical absorption measurements were made at room temperature with a Cary 5E spectrophotometer operating in transmission mode over the interval 200–1000 nm. Raw data were accumulated as absorbance and converted to absorption coefficient for presentation. Changes in optical absorption as a result of thermal annealing were done by heating the sample at 1 K/s in air to the desired temperature, allowing it to cool unaided to room temperature and re-measuring the absorption. Time lapse between final neutron irradiation and optical absorption measurements was approximately one month, whereas for X-irradiated samples the time lapse was approximately 1 h. The X-ray dose for optical absorption studies was 8.75 kGy and the neutron fluence was 1.1×10^{19} n/m^2.

2.3. Radioluminescence

Radioluminescence (RL) spectra were obtained both at room temperature and 10 K by placing the sample onto a silver holder inside a continuous-flow liquid helium cryostat, evacuating the system (10^{-6} Torr), irradiating with X-rays, and detecting the emission with a cooled, charge-coupled device (CCD) detector. X-radiation entered the sample chamber through a beryllium window and RL was collected by an optical fiber, which was positioned at an angle of 90° with respect to the X-ray beam. The emitted light was transmitted via the fiber to the entrance slit of a 0.3-m monochromator and onto the CCD detector. RL spectra were recorded in the interval 200–700 nm and were not corrected for system nonlinearities. Long-pass optical filters were employed to reject second order emission. After establishing that the region of RL emission peaked near 300 nm, final RL spectra were recorded with a 300-nm blazed grating having 150 grooves/mm. The monochromator entrance slit width was 100 μm and the CCD integration time was 15 s.

2.4. Thermally stimulated luminescence

A Harshaw Model 3500 reader was used to measure TSL glow curves over the temperature range 300–675 K. Immediately following X irradiation (11.55 kGy) at 295 K, samples were heated at a linear rate of 1 K/s to 675 K and the resulting glow curves were recorded. Neutron-irradiated samples were measured following a one month time lapse. Nitrogen gas flowed through the sample chamber during the heating cycle to minimize silver planchet oxidation and thereby reduce blackbody emission. Relative to the sample's TSL signal, blackbody emission at 675 K was negligible and was not subtracted from the raw emission.

3. Experimental results

3.1. Pre-neutron irradiation

Optical absorption, RL and TSL measurements were made on as-received CaF_2 crystals to search for impurities and to establish a baseline for comparison with neutron-irradiated specimens. Fig. 1 shows optical absorption of as-received and X-irradiated (8.75 kGy) CaF_2 measured at room temperature. The as-received specimen exhibits minimal absorption throughout the entire range 200–1000 nm. An upturn in the absorption below 400 nm is likely associated with the onset of band edge absorption (CaF_2 band gap ~12 eV) and Rayleigh scattering. In contrast, X-irradiated CaF_2 shows significant absorption with maxima at 255, 330, 385, 460, 510, 555, and 735 nm.

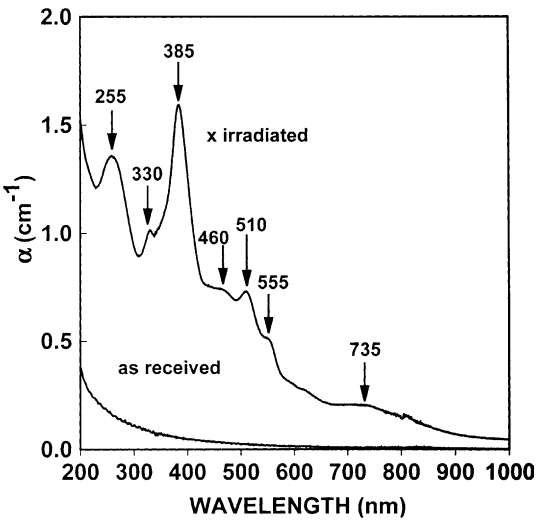

Fig. 1. Room temperature optical absorption of as-received and X-irradiated (8.75 kGy) CaF_2.

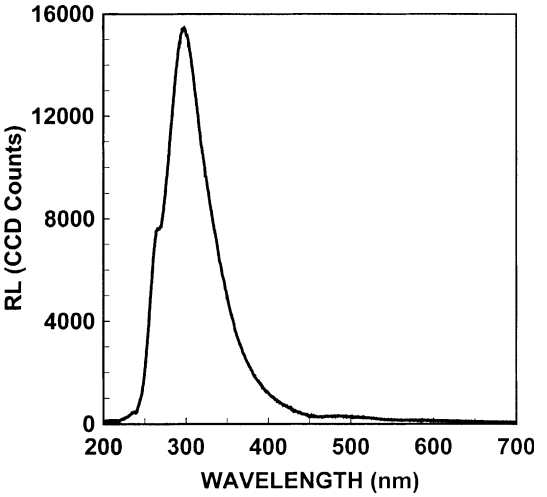

Fig. 2. Radioluminescence of as-received CaF_2 measured at 295 K.

The RL spectrum of as-received CaF_2 measured at 295 K is given in Fig. 2. A similar spectrum, but with enhanced intensity, was observed at 10 K. Intense emission occurs at 297 nm with secondary maximum at 265 nm. This spectrum was taken on pristine CaF_2 during a 15-s X-ray exposure (total dose = 26.25 Gy). Growth of optical absorption bands during this small exposure is minimal and therefore self-absorption of RL is negligible.

Fig. 3 shows the TSL glow curve of CaF_2 X-irradiated at 295 K to a total dose of 11.55 kGy and heated to 640 K at a linear rate of 1 K/s. The thick solid

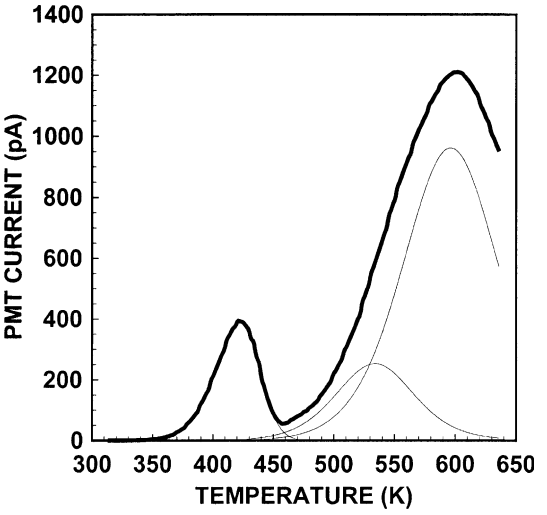

Fig. 3. TSL glow curve of CaF_2 X irradiated (11.55 kGy) at 295 K and heated at a linear rate of 1 K/s. The bold solid line is experimental data and the thin solid lines are fits to theory.

Table 1
X-ray-induced TSL glow-peak parameters ($\beta = 1$ K/s)

Peak T (K)	E (eV)	s (s^{-1})	ℓ
422.5	0.97	1.8×10^{10}	1.1
534.0	0.98	5.7×10^{7}	1.6
596.2	1.00	7.1×10^{6}	1.6

line is the experimental curve showing peaks at 423 and 596 K. The thin solid lines are best fits to the general-order kinetics expression developed by Chen [8]. Notice that the best fit is obtained with three peaks having maxima at 422.5, 534.0, and 596.2 K. The fitting procedure has previously been discussed by Cooke et al. [9]. The general-order TSL expression relating intensity $I(T)$ as a function of temperature to the frequency factor s, thermal activation energy E, order of kinetics, and constant heating rate β, is

$$I(T) = sC \exp\left(-\frac{E}{kT}\right) \times \left[(\ell - 1)\frac{s}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{k\theta}\right)\mathrm{d}\theta + 1\right]^{-\ell/(\ell-1)}, \quad (1)$$

where C is a constant related to luminescence efficiency, k is Boltzmann's constant, and θ is a variable of integration. The best-fit parameters are given in Table 1.

3.2. Post-neutron irradiation

Fig. 4 shows CaF_2 optical absorption following neutron irradiation at room temperature along with the result obtained by annealing the neutron-irradiated sample to 675 K and again measuring absorption at room temperature. Optical absorption of pristine CaF_2 is shown for comparative purposes. Absorption peaks occur at 255, 385, 455, 550, and 660 nm as a result of neutron irradiation (fluence $= 1.1 \times 10^{19}$ n/m^2). Thermal annealing significantly reduces the neutron-induced absorption with only the 385 nm peak remaining, albeit greatly reduced in intensity.

A comparison of neutron- and X-ray-induced optical absorption is shown in Fig. 5. The spectra are quite similar in peak structure with the major difference being the absence of the 510- and 330-nm peaks in the neutron spectrum.

The neutron-induced TSL glow curve is shown as the dotted line in Fig. 6. A well-resolved peak occurs near 480 K with weaker peaks near 550 and 605 K and at least one peak above 675 K. The solid line is a fit of Eq. (1) to the experimental glow curve with values $T_m = 479.3$ K, $E = 1.66$ eV, $s = 4.1 \times 10^{16}$ s^{-1}, and $\ell = 1.5$. Attempts to fit the weaker peaks were unsuccessful.

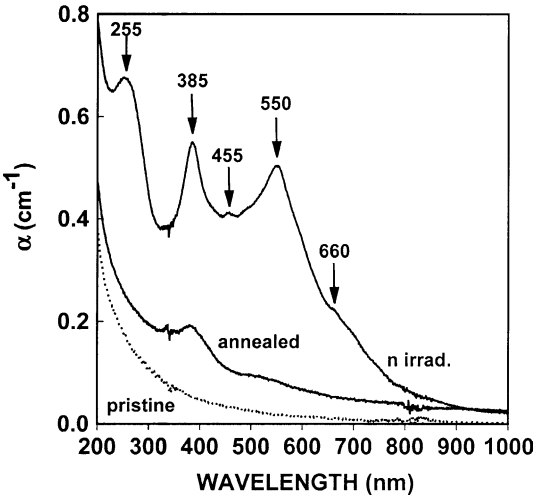

Fig. 4. Room temperature optical absorption of as-received and neutron-irradiated (1.1×10^{19} n/m^2) CaF_2. The curve labeled 'annealed' was obtained after heating the sample to 675 K, cooling to room temperature and re-measuring the absorption.

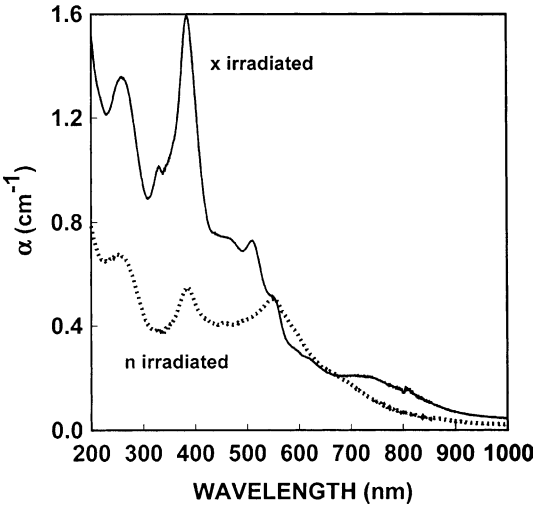

Fig. 5. Comparison of the X- and neutron-irradiated optical absorption spectra.

Comparison of the neutron-induced glow curve to the X-ray-induced curve requires caution. During neutron irradiation the sample temperature is expected to increase several tens of degrees above room temperature, which could skew the subsequent glow curve by removing trapped charges that normally contribute to its initial rise. Note that the intensity of the neutron-irradiated glow curve is more than four-orders-of-magnitude greater than the X-ray-induced one.

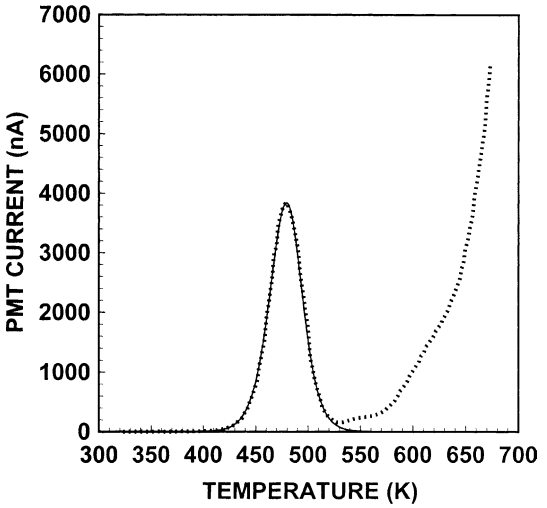

Fig. 6. TSL glow curve of CaF_2 neutron-irradiated (1.1×10^{19} n/m^2) at room temperature and heated at a linear rate of 1 K/s. The dotted line is experimental data and the thin solid line is a fit to theory.

By measuring the TSL glow curve of the neutron-irradiated sample (Fig. 6), we have effectively annealed the sample to 675 K at a linear rate of 1 K/s. The optical absorption spectrum labeled 'annealed' in Fig. 4 was taken following this TSL measurement. Thermal annealing of an X-irradiated specimen showed similar results (see curve labeled '700 K' in Fig. 7). Unfortunately, we did not have an additional neutron-irradiated sample on which to conduct stepwise thermal annealing of the optical absorption spectrum. But, because of the similar results obtained in the initial thermal annealing of each sample, we assumed that stepwise thermal annealing of an X-irradiated sample would be similar to that of the neutron-irradiated specimen. Thus we conducted stepwise thermal annealing of the X-irradiated (11.55 kGy) sample.

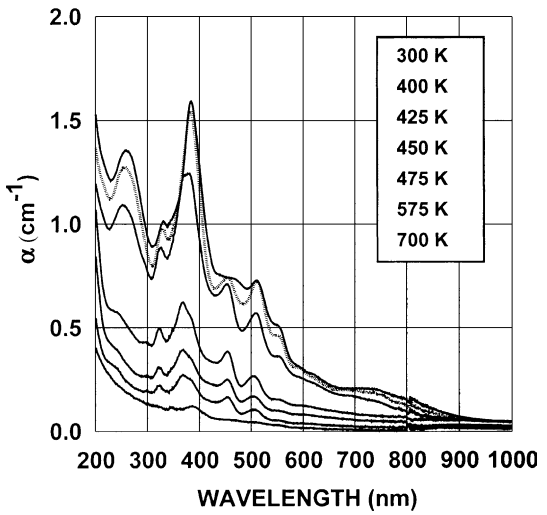

Fig. 7. Stepwise thermal annealing of X-irradiated (11.55 kGy) CaF_2. Samples were heated to the indicated temperatures, cooled unaided to room temperature and measured. The absorption spectra decrease systematically with increased annealing temperature.

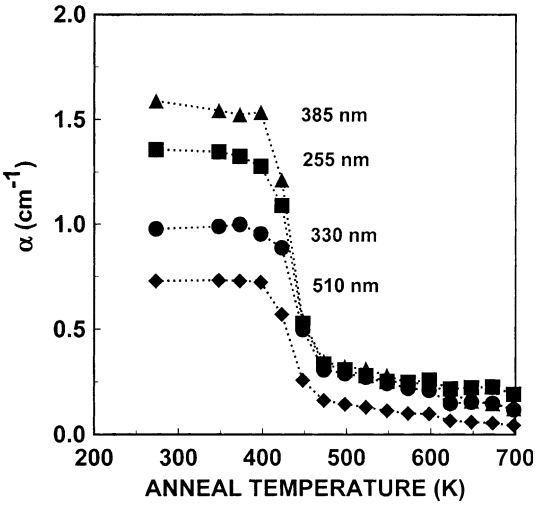

Fig. 8. Thermal annealing behavior of the four major absorption bands of Fig. 7. The precipitous drop near 425 K is coincident with the TSL glow peak at 423 K.

Fig. 7 shows representative effects of thermal annealing on the X-ray-induced optical absorption. Each spectrum was obtained after heating the sample at a linear rate of 1 K/s to the indicated temperature, cooling in ambient to room temperature and recording the spectrum. The absorption of the four main peaks as a function of annealing temperature is illustrated in Fig. 8 where we have included all experimental data points. A precipitous drop in each of the absorption peaks occurs between approximately 400 and 450 K, which brackets the TSL glow peak maximum of 423 K. This strongly suggests correlation between the glow peak and optical absorption, consistent with a similar observation previously noted by Atobe [6].

4. Discussion

As-received, crystalline CaF_2 exhibits excellent optical transmission in the spectral region 200–1000 nm with no indication of absorption peaks attributable to impurities or defects. However, X-ray excitation induces significant absorption with a spectrum characterized by well-resolved peaks at 255, 330, 385, 510 and 555 nm, along with additional weaker peaks. Previous results on X-irradiated CaF_2 show similar spectra. Bontinck [4] found peaks near 200, 225, 340, 400 and 580 nm, and

Kamikawa and Ozawa [5] noted the usual X-irradiated CaF_2 four-band absorption spectrum with peaks at 223, 333, 400 and 583 nm. These results are in reasonable agreement with the present data.

Considerable progress has been made in identifying the major absorption bands in CaF_2 and the results have been discussed by Hayes [3]. They conclude that F-band absorption occurs at 376 nm, which is near our measured absorption peak at 385 nm. The F-center in CaF_2 comprises an electron trapped at a fluorine vacancy, which, intuitively, should be readily produced by ionizing radiation. However, Bessent et al. [10] did not find significant F-center absorption in undoped CaF_2 for any irradiation temperature. Conversely, they found that significant coloration occurred only if the sample contained impurities that either acted as stable electron traps or gave rise to anion vacancies under irradiation. Our TSL data indicate the presence of electron trapping sites (see Fig. 3), and we conclude that the 385 nm absorption peak is associated with F-center absorption.

Other absorption bands that have been identified in CaF_2 include the self-trapped hole (V_k center) [11], M and R centers [3]. The latter two centers are also referred to as F_2 and F_3 centers, respectively [12]. The V_k center comprises a hole stabilized between adjacent fluorine ions with an absorption band near 320 nm. And although we observe a peak at 330 nm in the X-ray-induced spectrum of Fig. 1, we are reluctant to assign it to the V_k center because this center is known to thermally decay above 140 K. The 297-nm peak in the RL spectrum of Fig. 2 is due to self-trapped excitons, which consist of electrons trapped in the positive potential of V_k centers ($V_k + e^-$) [13]. Although this demonstrates existence of V_k centers at room temperature, it is important to note that they only occur during continuous irradiation and are not stable at room temperature when exposure is terminated. Moreover, as discussed below, the thermal annealing behavior of the 330-nm peak follows that of the other major peaks, which are identified as electron rather than hole traps.

The M center consists of a pair of F centers residing along either the $\langle 1\,0\,0\rangle$ or $\langle 1\,1\,0\rangle$ direction with maximum optical absorption near 520 nm. Three nearest F centers comprise the R center, which exhibits maximum optical absorption near 670 nm. Based on these known defects and the data of Fig. 1, we suggest that the 510- and 660-nm peaks are associated with the M and R centers, respectively.

Beaumont et al. suggest that 'pure' CaF_2 is not amenable to radiation induced absorption, but is readily damaged if it contains trace amounts of trivalent impurities such as rare-earth ions [11]. These putative impurities would be easily ionized yielding electrons that could become trapped at intrinsic defects (anion vacancies, for example) thus creating color centers (F, M, R, V_k, etc.). Alternatively, it is well known that alkali halides and alkaline earth fluorides are very susceptible to radiolysis. [14–16] This process involves the formation of atomic or ionic defects through a series of reactions initiated by electronic excitation. The formation of F and F-aggregate centers in CaF_2 is likely due to this mechanism rather than ionization of impurities because optical absorption spectra on as-received samples give no evidence for the existence of impurities.

There is similarity between the neutron and X-ray induced absorption curves as shown in Fig. 5. Missing in the neutron absorption spectrum is the unidentified band at 330 nm as well as the 460- and 510-nm bands. Similar results were obtained by Bontinck [4] in crystals exposed to reactor neutrons at room temperature, and by Kamikawa and Ozawa [5] in samples exposed to reactor neutrons at liquid nitrogen temperature. The latter authors concluded that the F band was not observed, and, further, that a band at 535 nm was characteristic of neutron irradiation. The width of the 550 nm neutron-induced band in the present data suggests that it is comprised of more than one band and is likely a superposition of the 510- and 555-nm bands observed in the X-ray spectrum. We suggest that this band is related to M centers and is not unique to the neutron absorption spectrum.

We now consider the thermal stability of F and F-aggregate centers. Thermal annealing (Figs. 7 and 8) shows a precipitous drop in optical absorption near 425 K that is coincident in temperature with the 423-K TSL glow peak. This peak is attributed to the release of trapped electrons rather than holes due to the latter's high mobility above room temperature [3]. Thermal decay of the four main absorption peaks is then due to release of trapped electrons, consistent with the notion that they are associated with F and F-aggregate centers. The fact that they all decay within the same relatively narrow temperature range (~425–475 K) shows that the release of trapped electrons from putative F and F-aggregate centers occurs with nearly identical activation energies, viz., 0.97 eV.

5. Conclusions

The effects of 14-MeV neutron irradiation (1.1×10^{19} n/m^2) on single-crystal CaF_2 have been investigated by optical absorption, TSL, RL and thermal annealing techniques. For comparative purposes similar studies were also done on as-received and X-irradiated samples. Pristine CaF_2 exhibits very good optical transmission in the region 200–1000 nm, suggesting the absence of impurities. X irradiation (8.75 kGy) induces significant absorption with peaks at 255, 330, 385, 460, 510, 555, and 735 nm and maximum absorption coefficient near 1.6 cm^{-1}. Relatively weak TSL occurs in the X-irradiated

(11.55 kGy) specimen and is characterized by glow peaks at 423, 534 and 596 K.

Neutron irradiation induces optical absorption in CaF_2 that is characterized by a spectrum similar to the X-ray-induced one. Absorption peaks occur at 255, 385, 455, 550 and 660 nm with maximum absorption coefficient near 0.8 cm^{-1}. The neutron-induced TSL glow curve is relatively strong with peaks at 479, 550 and 605 K and indication of a peak above 675 K.

Both the X-ray- and neutron-induced absorption spectra can be thermally annealed. Stepwise annealing of the X-irradiated absorption spectrum shows a precipitous drop in absorption that is coincident with the glow peak maximum temperature. Therefore, we conclude that the major absorption peaks are associated with F and F-aggregate centers and that the corresponding TSL glow peak is an electron trap.

The presence of TSL glow peaks and the ease with which color centers are induced by either X or neutron irradiation show that CaF_2 is not a good final optic window material for fusion energy applications.

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