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Irradiation effects in CaF$_2$: ZnO nanostructured crystals

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Abstract. Effects of $\beta$, X, and UV radiation were studied in CaF$_2$: ZnO single crystals in which ZnO was embedded as nanoparticles. Absorption measurements of these crystals showed a steep increase below 250nm and a weak absorption peak at about 310nm. After prolonged $\beta$ irradiation, additional absorption bands were recorded at 395 and 595nm. The irradiated samples showed during heating several thermoluminescence (TL) peaks. Samples which had been exposed to $\beta$-irradiation at RT and subsequently illuminated at LNT with 390nm light showed during re-heating to RT several TL peaks that are attributed to a process of photo-transferred TL (PTTL). Main photoluminescence (PL) emission bands were recorded at 320 and 340nm with excitation maxima near 250 and 300nm. These emission bands were also observed during X-irradiation as well as additional emission bands near 355 and 400nm. In pre-irradiated samples, a 320nm luminescence band could also be excited by 395nm light and is attributed to a process of photostimulation. The stimulation maxima of the OSL and PTTL in the 390nm region are apparently due to the observed absorption band at 395nm induced by the $\beta$-irradiation. The fact that some of the same emission bands appeared in the XL, PL, TL and OSL of this crystal indicates that the same luminescence centers are involved in these emissions.

1. Introduction

Radiation effects and optical properties of alkaline-earth fluorides (AEF) have been studied for several decades [e.g.:1-3]. These broadband crystals are transparent in a wide spectral range from the infrared (IR) to the vacuum ultraviolet (VUV) region and are therefore widely used as optical materials. Special attention has also been given to alkali halide fluorides (AHF) and AHF doped with rare-earth (RE) ions. The trivalent RE doped AEF contain F interstitial ions, compensating for the excess charge of the trivalent ions, which occupy sites of divalent cations in the crystal lattice. The F interstitial ions are assumed to be the dominant carriers in these doped fluoride crystals. These fluorides are of interest from both the points of view of basic and applied research. Some mixed fluorides are used as efficient radiation detectors and dosimeters [e.g.:4, 5]. Much attention has recently also been given to the applications of various rare-earth doped fluorides for computed radiography (CR). Computed radiography using photostimulable phosphor
storage media allows the combination of highly advanced photographic technology with digital computer techniques. Optically stimulated luminescence (PSL) is a process where exposure to high-energy radiation (X, β or VUV) results in the accumulation of stored charges such as F-centers. These stored charges can then be photostimulated to the conduction band using, for example, low-energy visible or near-infrared photons where they may recombine with holes to produce a near-UV or visible OSL emission. This digital X-ray imaging technique is one of the primary candidates to replace the long-established screen-film radiography [6]. Zinc oxide is a direct band gap semiconductor with band gap energy of 3.37 eV at room temperature (RT). The large exciton binding energy (60 meV) ensures efficient excitonic emission at room temperature. Therefore, the luminescent properties of ZnO have attracted considerable attention due to its potential application in ultraviolet light emitting devices and in flat panel displays as a low voltage phosphor. The developments in fabrication techniques of nanometer-sized semiconductors have further stimulated the studies on ZnO. In recent years, a variety of ZnO nanometer or micrometer structures including belts, rods, and tubes has been reported [e.g.:7, 8]. More recently, devices such as a ZnO heterostructured light emitting devices (LED) and field-effect transistors based on ZnO nanowires have been demonstrated. The structural, optical, electrical properties and applications of nanostructured ZnO have been summarized in some reviews [e.g.:9]. High quality ZnO nanoparticles can be synthesized by encapsulating them into dielectric materials [10, 11]. For example, high-quality ZnO nanocrystals have been fabricated by zinc ion implantation into a CaF$_2$ single-crystal substrate followed by thermal annealing from 300 to 700°C; a very strong ultraviolet near-band-edge emission was observed from 372 to 379nm [10]. It has recently also been found that a green luminescence band related to oxygen vacancies, which appears in ZnO raw powders, disappears when they are dispersed in a thin KI crystal [11]. This is probably due to I$^-$ ions supplied from the KI crystal which fill in the oxygen vacancies in the ZnO particle. As a result, a lot of I$^-$ ions acting as donor impurities in ZnO may exist near the interface between the ZnO particle and the KI matrix. Consequently, ZnO nanoparticles in KI crystals have strong luminescence from the free and bound excitons [11]. Nanoparticles encapsulated in dielectric matrices may also find applications for optical storage and medical imaging [e.g.:12]. Up to now, TL was reported in relatively few studies on nanoparticles [e.g.:13, 14].

In the present work optical properties and irradiation effects were studied in CaF$_2$: ZnO single crystals in which ZnO was embedded as nano-particles. Optical absorption, thermoluminescence (TL) as well as luminescence induced by X-rays (XL) and by monochromatic UV light (PL) were measured. In pre-irradiated samples also optically stimulated luminescence (OSL) and phototransferred-thermoluminescence (PTTL) were investigated. Results were compared to those obtained in nominally pure CaF$_2$ crystals.

2. Experimental Techniques

ZnO nanocrystals were embedded into CaF$_2$ single crystal; CaF$_2$: ZnO single crystals were fabricated by zinc ion implantation of ~160 keV, 1x10$^{17}$ ions/cm$^2$ into a CaF$_2$ (111) single-crystal followed by thermal annealing up to 700°C [10]. The nominally pure CaF$_2$ crystals used for the measurements were from Harshaw. The X-irradiations were performed with a W-tube (40kV, 15mA) and the β-irradiations with a $^{90}$Sr source of a 1.5 Gy/min dose-rate. The TL measurements from RT up were carried out in a TL compartment flushed by N$_2$ gas; the heating rate above RT was 5K/sec. For the low temperature TL and PTTL measurements the samples were kept in a liquid nitrogen vacuum cryostat and heated at a rate of 20K/min. Further experimental details have been given elsewhere [15].

3. Results and Discussion

3.1. Optical Absorption
The optical absorption of the CaF$_2$: ZnO single crystals was measured before and after exposure to $\beta$ irradiation at RT. Fresh samples showed an increase of absorption in the UV toward 200nm while pure CaF$_2$ crystals are transparent in a broad wavelength region from the near IR up to about 10eV. After prolonged $\beta$ irradiation at RT additional absorption bands appeared in the CaF$_2$: ZnO samples near 400 and 580nm, but were not recorded in pure CaF$_2$ samples. Absorption bands at 3.1 and 2.4 eV have, however been reported previously in ZnO and were ascribed to Zn$_i^+$ (interstitial ions) and F-centers respectively [16]; the radiation induced bands near 400 and 580nm reported here may be due to the same defects. These additional bands could be thermally bleached by heating to about 800K and the absorption curve of the annealed sample regained the shape of the fresh sample before the exposure to irradiation (Fig. 1).

3.2. Thermoluminescence
During heating of a $\beta$ irradiated sample from 300 to about 800K a strong TL was recorded and the main TL peaks appeared in the CaF$_2$: ZnO crystals near 430 and 550 K. The TL was compared to that of nominally pure CaF$_2$ crystals and to that of the well known dosimetric material TLD-100 (LIF: Mg, Ti); the results are shown in Figure 2. It can be seen that the TL sensitivity of the main peak of CaF$_2$: ZnO near 430K is about the same as that of the main TL peak in pure CaF$_2$ and twice than that of the main TL peak in TLD-100.

After X-irradiation at LNT, TL peaks appeared in the CaF$_2$: ZnO crystals at about 175 and 260K (Fig. 3a). The PTTL of a sample that had previously been exposed to $\beta$ radiation at RT and subsequently illuminated with 395nm light at LNT, was recorded during heating from LNT to RT and is shown for

![Figure 1. Optical Absorption of a CaF$_2$: ZnO crystal: (a) after exposure to $\beta$ irradiation (b) after subsequent annealing to ~800K (The same absorption was recorded for a fresh sample before exposure to $\beta$ irradiation).](image1)

![Figure 2. Comparison of the TL sensitivities of: a) CaF$_2$: ZnO crystal, b) nominally pure CaF$_2$ crystal and (c) TLD-100. (All samples after exposure to equal $\beta$ doses of 90Gy. All data are normalized for a unit mass of the various materials).](image2)
3.3 Luminescence.
The luminescence emitted during X-irradiation (XL) was measured and is given by curve (a) of Fig. 5 and the luminescence emitted at the TL peak near 430K by curve 5(b). The 420nm band and the component at about 475nm that appeared in the TL emission were also recorded in the XL; the main XL emission band appeared, however, at 320nm. It may be noted that a broad emission band near 300nm has previously been recorded in the luminescence of pure and rare-earth doped CaF$_2$ crystals and was ascribed to an X-ray excited self trapped exciton [3]. Photoluminescence (PL) could also be excited by UV light and a main emission band appeared at the same wavelength of 320nm. Excitation spectra of these PL bands showed maxima at 240, 290 and 305nm. Emission and excitation spectra of CaF$_2$: ZnO are given in Fig. 6. The 340nm emission band has previously been assigned to either an F-center or to some unidentified impurity level [10].

3.4 Phototransferred - Thermoluminescence and Optically stimulated Luminescence
In samples that had previously been exposed to ionizing radiation, luminescence could be excited by illumination with wavelengths that could not excite any PL in non-irradiated samples and even by wavelengths longer than those of the emitted luminescence. These emissions are attributed to a process of optical stimulation. Optically stimulated luminescence (OSL) is a process where exposure to high-energy radiation results in the accumulation of carriers at traps such as color centers. These trapped carriers can then be stimulated by visible or near UV light and produce a measurable OSL emission. In Fig. 7, the emission spectrum of a CaF$_2$: ZnO crystal is shown. The main 320nm OSL band appeared at the same wavelengths as the XL and PL emission bands. An emission band near 320nm has recently been recorded in the synchrotron exited PL of ZnO single crystals as well as in nanostructed ZnO thin films and it has been suggested that this emission band is probably due to the radiative recombination of excitons in the surface of the ZnO particles. [17, 18, 19] The stimulation spectrum of the OSL emission was also measured in the present work and showed a maximum at 395nm (Fig. 8). This stimulation maximum coincides with the radiation induced absorption band at the same wavelength (curve (a) of Fig. 1) and is apparently due to an energy level of a radiation induced defect. This was supported by the finding that the OSL could not be stimulated by 395nm light in non-pre-irradiated samples and that in the pre-irradiated samples the emission was optically bleached by prolonged illumination with 395nm light. The OSL could also be thermally bleached by heating to ~800K. The fact that some of the same emission bands appeared in the XL, PL, TL and OSL of this crystal indicates that the same luminescence centers are involved in these emissions.

**Figure 5.** Emission spectra of: a) XL at RT and b) TL measured in CaF$_2$: ZnO at the peak near 430K.

**Figure 6.** PL excitation and emission spectra of a CaF$_2$: ZnO crystal at RT: a) and b) excitation spectra of the 320 and 340nm emission, respectively; c), d), and e) emission spectra recorded during excitation with 305, 300 and 295nm, respectively.
Samples that had previously been exposed to ionizing radiation at RT and were subsequently illuminated at LNT with near UV or visible light of appropriate wavelengths showed during heating from LNT to RT a TL emission that could not be excited by these wavelengths in non pre-irradiated samples. These glow peaks are attributed to a process of optical stimulation or photo-transfer (PTTL). In this process, carriers that were trapped by the ionizing radiation in deep traps are then optically stimulated at lower temperature and transferred to shallower traps, which are not stable at the temperature of exposure to ionizing irradiation. PTTL glow peaks may appear during re-heating, when the carriers are thermally released from the shallow traps and recombine radiatively with carriers of opposite sign. The wavelength of 395nm, that was most efficient for the stimulation of the OSL in the CaF$_2$: ZnO crystals, was also found to be most efficient for the excitation of the PTTL in the same crystals. The main PTTL peak appeared at the same temperature of 260K as the low-temperature TL peak, indicating that the PTTL peak is due to the same trapping level as this TL peak [see curve (b) of Fig. 3]. The spectral composition of the TL emission was also measured in the course of this study. The emission spectrum recorded at the TL near 430K is shown by curve (b) of Fig. 5. The main broad spectral band appeared near 500nm and weaker ones at about 240, 420 and 580nm. The main broad band near 500nm appeared to be composed and could be resolved into several narrow bands.

![Figure 7. OSL emission spectrum of a pre-irradiated CaF$_2$: ZnO crystal at RT.](image)

![Figure 8. Stimulation Spectrum of the 320nm OSL emission band in a CaF$_2$: ZnO crystal after β-irradiation at RT.](image)

4. Summary

- The exposure to prolonged β radiation resulted in the appearance of additional absorption bands at about 400 and 600nm.
- During heating from RT, the irradiated crystals showed a TL peaks near 430K.
- The dependence of intensity of this TL peak on the radiation dose was nearly linear to about 1000Gy, and the TL sensitivity was about twice that of TLD-100.

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In crystals that had previously been exposed to ionizing radiation notable PTTL as well as OSL could be excited by illumination with wavelengths that could not excite any TL or PL in non-irradiated samples.

The main low-temperature TL peak and the main PTTL peak appeared both at 260K, indicating that this TL peak and the PTTL are due to the same trapping level.

The wavelength of 395nm was most efficient for the stimulation of both the PTTL and OSL. This stimulation maximum is apparently due to the radiation induced absorption band at the same wavelength (see Fig. 1a) which is stable to about 800K.

The fact that the TL, XL, PL and OSL show some of the same emission bands indicates that the same luminescence centers are involved in these emissions.

References