

## LUMINESCENCE OF CsGd<sub>2</sub>F<sub>7</sub> CRYSTALS

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**Abstract**—Optical and dosimetric properties of nominally pure CsGd<sub>2</sub>F<sub>7</sub> crystals and of CsGd<sub>2</sub>F<sub>7</sub> crystals doped with various concentrations of Pr<sup>3+</sup> ions were investigated. Effects of X,  $\beta$  and UV irradiation on these crystals were studied. Methods of optical absorption, X and UV excited luminescence, thermoluminescence (TL), phototransferred thermoluminescence and optically stimulated luminescence were used in these investigations. The dependence of the TL efficiency on the radiation dose was found to be linear up to 6 kGy for the 3 at.% Pr<sup>3+</sup> doped samples. The crystals containing from 0.3 at.% to 1.0 at.% of Pr<sup>3+</sup> ions were found to have the best TL sensitivity and the intensity of the main TL peak in these samples was more than two orders of magnitude higher than that of the pure crystals. The TL sensitivity of the CsGd<sub>2</sub>F<sub>7</sub>:Pr<sup>3+</sup> crystals was also compared with that of other commonly used TLD materials.

### INTRODUCTION

Fluoride crystals are the broadest band-gap alkali halides and are transparent in a wide spectral range from the IR to the vacuum UV (VUV) region. Therefore these crystals are widely used as optical materials. Optical properties and irradiation effects in pure and variously doped fluoride crystals have actively been studied for the past few decades from the viewpoint of both basic and applied research<sup>(1)</sup>. Most of the previous studies on irradiation effects and the formation of point defects concentrated on the effects of higher energy radiation, such as  $\gamma$ ,  $\beta$  and X rays; in relatively few works, effects of VUV radiation have been investigated<sup>(2,3)</sup>. Much interest has recently been given to the search into new promising materials, which can be used for radiation detectors and solid state dosimeters. In previous work, mainly thermoluminescence (TL) methods have been utilised for these studies. More recently methods of optically stimulated luminescence (OSL) and of phototransferred thermoluminescence (PTTL) also have been applied<sup>(4,5)</sup>. Some doped fluoride crystals, such as TLD-100 (LiF: Mg, Ti), are now frequently used for these purposes<sup>(6)</sup>.

In the present work the optical properties and effects of X,  $\beta$  and VUV irradiation were investigated in Pr<sup>3+</sup> doped CsGd<sub>2</sub>F<sub>7</sub> crystals. The effects were compared with those in nominally pure CsGd<sub>2</sub>F<sub>7</sub> crystals. Optical absorption, X luminescence (XL), photoluminescence (PL) and OSL as well as TL and PTTL were measured. The possible application of these crystals to solid state dosimetry was also investigated.

### EXPERIMENTAL TECHNIQUE

A series of CsGd<sub>2</sub>F<sub>7</sub> single crystals doped with Pr<sup>3+</sup> (from 0 up to 3.0 at. %) was grown by a direct tempera-

ture-gradient method. The crystals were obtained as a result of a reaction of caesium fluoride aqueous solutions with appropriate mixtures of 99.99% pure rare earth oxides under hydrothermal conditions at a temperature of 750 K and pressures of 100–150 MPa<sup>(7)</sup>. The X and the  $\beta$  irradiations were performed with a W-tube (40 kV, 15 mA) and a <sup>90</sup>Sr source of a 1.5 Gy.min<sup>-1</sup> dose rate, respectively. Both X and UV irradiations were carried out at various temperatures between 80 and 300 K. The TL measurements above RT were carried out in a TL compartment flushed by N<sub>2</sub> gas; the heating rate above RT was 5°C.s<sup>-1</sup>. For the low temperature absorption, luminescence and thermoluminescence measurements, the samples were kept in liquid nitrogen vacuum cryostat and for the TL measurements they were heated at a rate of 20°C.min<sup>-1</sup>. The PTTL and OSL were stimulated by monochromatic UV light at various temperatures between 80 and 400 K in samples which had previously been exposed to X or  $\beta$  radiation. The VUV irradiations were carried out with a one-metre normal-incident VUV monochromator and an H<sub>2</sub> arc lamp. The optical absorption was measured with a Cary 17 spectrophotometer. The PL, OSL, TL and PTTL measurements were taken with an Aminco-Bowman/2 luminescence-spectrometer.

### RESULTS AND DISCUSSION

#### Optical absorption

In the pure irradiated crystals, main sharp absorption bands were recorded at 200, 272 and 310 nm. The CsGd<sub>2</sub>F<sub>7</sub> crystals doped with Pr<sup>3+</sup> ions show additional absorption bands at 442, 468, 480, 575 and 585 nm and a steep increase of absorption below 225 nm.

#### X luminescence and photoluminescence

In all the samples, a 311 nm emission band appeared in the XL spectra. The Pr<sup>3+</sup> doped CsGd<sub>2</sub>F<sub>7</sub> crystals

showed additional narrow and apparently impurity related emission bands at 482, 492, 525 and 605 nm. XL emission spectra of a pure and of Pr<sup>3+</sup> doped samples at RT are shown in Figure 1. The PL emission showed essentially the same main bands and the same differences between the pure and the Pr doped samples. The luminescence intensity of the doped samples is, however, markedly higher than that of the pure CsGd<sub>2</sub>F<sub>7</sub> crystals. The 311 nm PL emission has in all samples a main excitation maximum near 275 nm; this wavelength caused in the doped crystals also the excitation of some other emission bands. In Figure 2 the PL emission spectra of pure and doped samples excited by the 275 nm UV light at LNT are shown. The sharp minima in the emission spectrum of the doped sample seem to be due to the self-absorption by the Pr<sup>3+</sup> impurity ion at these wavelengths.

The impurity related PL emission bands in the Pr doped crystals have additional excitation maxima, in particular at 441, 450, and 468 nm. The intensity of all

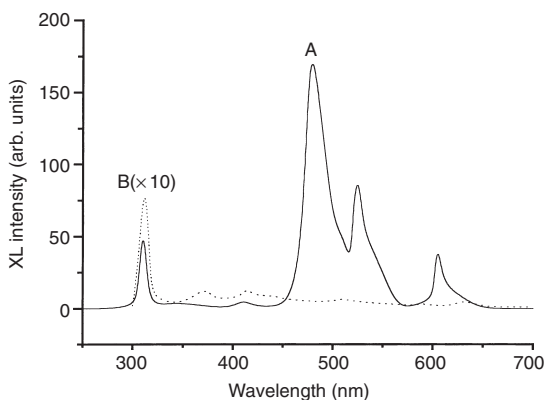


Figure 1. XL spectra of: (A) a 3 at.% Pr<sup>3+</sup> doped CsGd<sub>2</sub>F<sub>7</sub> crystal and (B) a pure CsGd<sub>2</sub>F<sub>7</sub> crystal at RT.

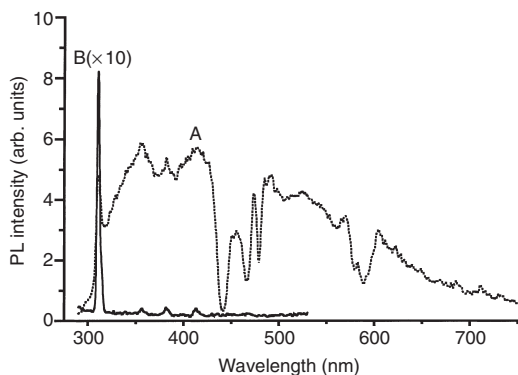


Figure 2. PL spectra excited by 275 nm UV light of: (A) a 3 at.% Pr<sup>3+</sup> doped CsGd<sub>2</sub>F<sub>7</sub> crystal and (B) a pure CsGd<sub>2</sub>F<sub>7</sub> crystal at LNT.

the emission bands, except the 525 nm band, rises during cooling from RT to LNT by a factor of two to three. Prolonged X or β irradiation caused a decrease of the 311 nm emission band in the Pr<sup>3+</sup> doped samples but the original intensity is restored after heating to about 600 K.

### Thermoluminescence

There are main TL peaks at about 220 and 410 K in all the X or β irradiated samples and additional ones at 260 and 428 K are observed only in the Pr<sup>3+</sup> doped samples. In the Pr<sup>3+</sup> doped samples TL can be excited with monochromatic VUV radiation in the spectral region between 110 and 190 nm. Optimal excitation efficiency in this region is reached near 150 nm; the excitation spectrum of a pure CsGd<sub>2</sub>F<sub>7</sub> crystal is shown in Figure 3. In the doped crystals TL can also be excited with the UV light at the tail of the absorption edge near 225 nm.

The TL emission of all the samples showed the same main 311 nm band and in the doped crystals appeared additional impurity related bands at 482, 525, 605, and near 700 nm, which were also observed in the XL and in the PL. After X irradiation at LNT, notable phosphorescence was recorded in the pure and the Pr<sup>3+</sup> doped samples. In Figure 4, emission spectra recorded at the LNT phosphorescence and at the main 410 K glow peak are given. In CsGd<sub>2</sub>F<sub>7</sub>:Pr<sup>3+</sup> crystals, which had previously been exposed to X or β radiation at RT, both PTTL and OSL could be stimulated with the 310 nm UV light at LNT.

### Dosimetric properties

The dependence of the TL efficiency on the Pr<sup>3+</sup> concentration was measured. The intensity of the main TL peak is maximal in the samples containing from 0.3 at.% to 1.0 at.% Pr<sup>3+</sup> and is higher by a factor of 300 than

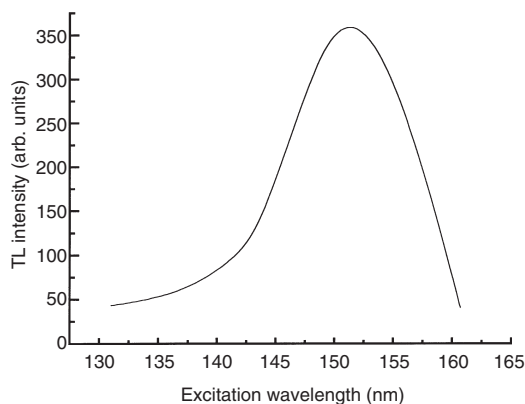


Figure 3. Excitation spectrum of TL in the CsGd<sub>2</sub>F<sub>7</sub>:Pr<sup>3+</sup> crystal excited by monochromatic VUV radiation at RT.

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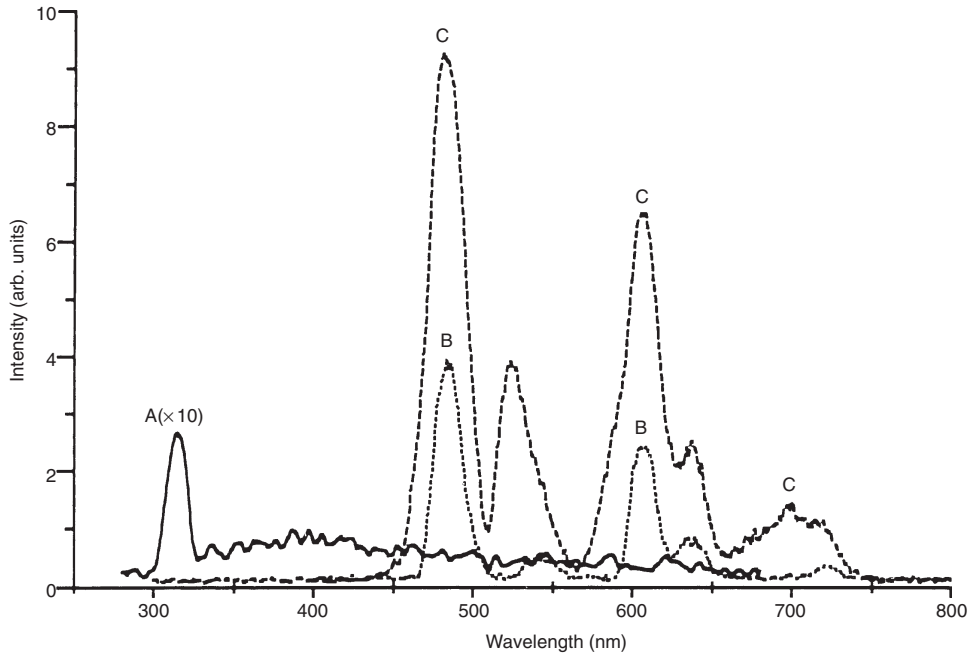


Figure 4. Emission spectra of (A) a pure  $\text{CsGd}_2\text{F}_7$  crystal, measured during phosphorescence decay at LNT; (B) a  $\text{CsGd}_2\text{F}_7:\text{Pr}^{3+}$  crystal, measured during phosphorescence decay at LNT; and (C) a  $\text{CsGd}_2\text{F}_7:\text{Pr}^{3+}$  crystal, measured at the 410 K TL peak.

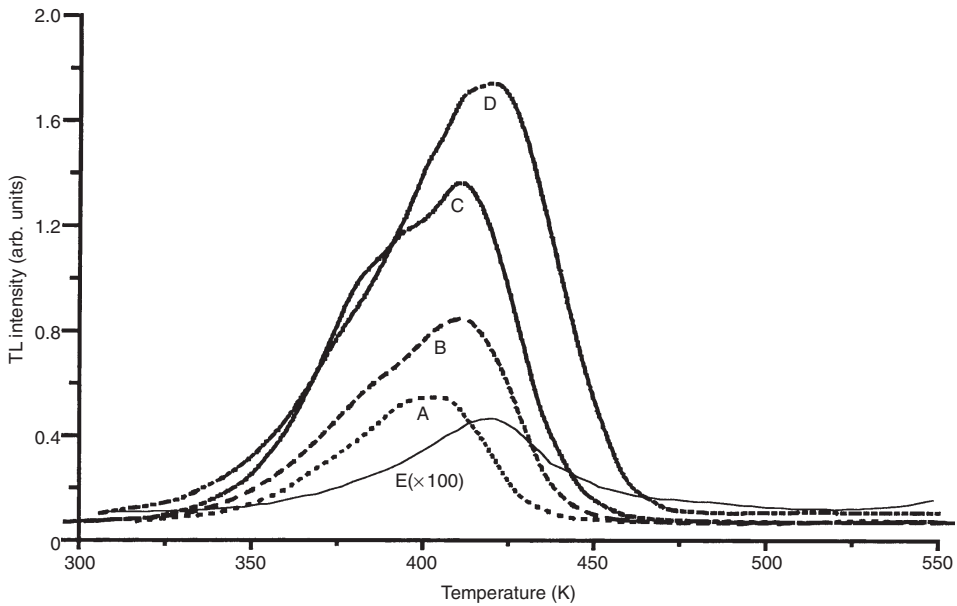


Figure 5. TL spectra excited by a constant  $\beta$  dose for the  $\text{CsGd}_2\text{F}_7$  crystals containing different  $\text{Pr}^{3+}$  concentrations of (A) 3.0, (B) 2.0, (C) 0.3, (D) 1.0 at.%  $\text{Pr}^{3+}$  and (E) for a pure  $\text{CsGd}_2\text{F}_7$  crystal at RT.

in the pure crystals (Figure 5). The TL sensitivity of the CsGd<sub>2</sub>F<sub>7</sub>:Pr<sup>3+</sup> crystals has also been compared to that of other commonly used TLD materials and was found to be of the order of the known LiF: Mg, Ti (TLD-100) phosphor. The main TL peak of the CsGd<sub>2</sub>F<sub>7</sub>:Pr<sup>3+</sup> crystals at 410 K is also well above room temperature and the emission bands of the main TL peaks are located in a convenient spectral region where most of the standard photomultipliers are sensitive. The effects of previous irradiation can be annealed by heating to an easily attainable temperature of about 700 K, which is of importance for repeated use of the same sample in additional measurements. The repeated use of a sample

may, however, be limited by taking into account that the crystals become brittle after heating. The dependence of the TL intensity on the irradiation dose for the CsGd<sub>2</sub>F<sub>7</sub>:Pr<sup>3+</sup> crystals has also been measured and was found to be linear in a wide range up to 6 kGy for the 3at% Pr<sup>3+</sup> doped samples. This is of importance for application of the materials of such a type in TL dosimeters.

#### ACKNOWLEDGEMENTS

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