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Suppression of Afterglow in Microcolumnar CsI:Tl by Codoping With Sm²⁺: Recent Advances

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Abstract

Microcolumnar CsI:Tl remains a highly desirable sensor for digital X-ray imaging due to its superior spatial resolution, bright emission, high absorption efficiency, and ready availability. Despite such obvious advantages, two characteristic properties of CsI:Tl undermine their use in clinical and high speed imaging: a persistent afterglow in its scintillation decay, and a hysteresis effect that distorts the scintillation yield after exposure to high radiation doses.

In our earlier work we have discovered that the addition of 0.05 to 0.5 mol percent of Sm²⁺ to crystals of CsI:Tl suppresses their afterglow by a factor of up to 50, even when subjected to a very high exposure of 120 R. This additive also diminishes hysteresis by an order of magnitude, which is a major accomplishment. Consequently, our work is now focused on developing codoped microcolumnar CsI:Tl, Sm films that can potentially combine excellent properties of the current state-of-the-art CsI:Tl films with the reduced afterglow and hysteresis observed in codoped crystals. While our earlier attempts in CsI:Tl, Sm film fabrication, reported at the previous IEEE meeting, demonstrated obvious advantages of the approach, the recent work has succeeded in producing films that show improvement by at least a factor of 7 in afterglow and 150% in brightness compared to the standard CsI:Tl films. We report these important results in this paper, along with other recent advances in film growth and new imaging results.

Index Terms

Scintillator characterization; scintillators

I. Introduction

Scintillation detectors are used in a wide variety of nuclear and medical applications. The medical community is particularly interested in new fast scintillators with high density and high light output for high speed imaging applications such as computed tomography (CT), diagnostic X-ray imaging [1], [2], positron emission tomography (PET), and single photon emission tomography (SPECT). While a wide choice of new scintillators is now available, CsI:Tl remains a highly desirable material due to its excellent properties, low cost, and easy availability [3]. CsI:Tl has found extensive use in nuclear and medical imaging applications because of its high conversion efficiency (64,000 photons/MeV), rapid initial decay (680 ns), emission in the visible range (540 nm) [4], [5] and a cubic structure that allows fabrication into microcolumnar films. It has a relatively high density (4.53 g cm³), high atomic number (Z = 54), and is completely transparent to its own emitted light. CsI:Tl is the material of choice for many applications, such as radiological and nuclear imaging in

medicine and industry, X-ray and γ -ray spectroscopy, homeland security and research applications.

Despite its obvious advantages, however, CsI:Tl has two characteristic properties that undermine its use in clinical and high-speed imaging: the presence of an afterglow component in its scintillation decay, and a hysteresis effect that causes non-deterministic change in its scintillation yield after exposure to high radiation doses. Although the initial decay has a characteristic time of 680 ns [4], its residual afterglow at 2 ms after the excitation can be as high as 5% of the peak value, depending on the intensity and duration of the excitation pulse. This causes pulse pileup in high count-rate applications, reconstruction artifacts in CT applications, and problems of reduced contrast and image blurring in high-speed X-ray imaging [4]–[6]. The hysteresis effect can either increase or decrease the light yield during use, representing a substantial source of instability and hence noise. If the afterglow and hysteresis in CsI:Tl were significantly reduced, the material could be effectively used in many important modalities such as medical cone-beam or spiral CT, enabling improved performance with substantial reduction in cost.

To address these specific issues, we have been exploring the feasibility of suppressing the afterglow and hysteresis of CsI:Tl by chemical means. We discovered that the addition of a second dopant, Eu^{2+} , was capable of substantially reducing the afterglow exhibited by CsI:Tl crystal scintillators. Our observations [7] and theoretical analysis [8] indicated that Eu^{2+} ions introduce deep electron traps at the codopant sites, which divert electrons that had thermally escaped from shallow traps associated with thallium, thereby suppressing the delayed radiative recombination responsible for afterglow. This immediately made the material useful for applications such as high-speed radiography, from which it had earlier been excluded. Afterglow, however, is not a material constant, but a strong function of the duration of the excitation pulse, so that we find [9] that the suppressive capabilities of Eu^{2+} become progressively diminished as excitation is applied for longer and longer periods. Indeed, we see that while Eu^{2+} suppresses the afterglow following short (submicrosecond) X-ray pulses by as much as four orders of magnitude, it actually exacerbates the residual emission after long-term (> 1 second) excitation. This we have attributed to the fact that while Eu^{2+} is quite effective in scavenging the afterglow-generating carriers over the short term ($\approx 100\text{ms}$), it does not provide any means for draining them away; consequently, they ultimately escape (albeit more slowly and at a later time) to enhance (and even dominate) the longer-term afterglow [9].

In our most recent work [10], [11] we have successfully addressed this issue by utilizing Sm^{2+} instead of Eu^{2+} as the codopant. Sm^{2+} ions also introduce deep electron traps, providing a similar scavenging effect. But Sm^{2+} , unlike Eu^{2+} , also has a number of energy levels that fall within the band gap of CsI, providing a mechanism for nonradiative relaxation that Eu^{2+} lacks, thereby annihilating the offending carriers and preventing their subsequent escape to generate delayed emission [11]. Thus we find that the addition of Sm^{2+} ions to crystals of CsI:Tl, while not quite as effective in afterglow reduction under short pulse excitation, is at least ten times better than Eu^{2+} when X-ray exposure lasts longer than a second. Moreover, Sm^{2+} retains its superior performance as far out in time as we can measure, even when the total radiation dose exceeds 40 R. Such improved performance can make CsI:Tl, Sm a serious candidate for use in X-ray CT applications.

An additional benefit of Sm^{2+} is the salutary effect it has on *hysteresis*. This term refers to a troublesome tendency, exhibited by many scintillators, for their light yield to fluctuate as a function of their excitation history. In such cases the light yield may drift up or down by unpredictable amounts during prolonged exposure to radiation, causing the signal to vary during use and representing a significant source of instability or noise in the system. In

CsI:Tl, this instability (which runs on the order of 10% during protracted intense X-ray exposure) has been attributed to a relatively long-term filling of some of the deeper traps, thereby temporarily removing them as a loss mechanism to the prompt emission. Thus we find that Sm²⁺, by providing a means to minimize such long-term trapping, keeps the light yield stable within 0.5% with relatively little cost in total emission. This is a significant result, which shows improvement in the hysteresis by a factor of 20 compared to the standard CsI:Tl when subjected to a very high exposure of 120 R. These results and the detailed procedure for measurement have already been described in previous papers [9], [10].

But all the results we have just summarized were obtained on *single crystals* grown from the melt. For CsI:Tl films, three critical questions remain to be answered:

- Can high-quality microcolumnar films actually be fabricated by controllable vapor deposition techniques?
- Will such films actually exhibit afterglow-suppressive properties consistent with those exhibited by single crystals?
- How will the imaging capabilities of such films compare with those of conventional material?

We have already examined these questions in a previous report [12]; it is the purpose of this paper to present further work and recent advances in these areas.

II. Film Deposition and Morphology

Although crystals of CsI:Tl, Sm have demonstrated highly favorable results, the use of this new material for high speed, high resolution X-ray imaging is possible only if the material can be grown in the form of microcolumnar films that exhibit similar scintillation properties as the codoped crystal. Moreover, the deposition process had to be controllable and reproducible, or the results of occasional successes would have no practical significance. This we accomplished through a proprietary process involving co-evaporation of the constituent iodides. Controlling the respective dopant concentrations was a major challenge, as the vapor pressures of CsI, TlI and SmI₂ differ by several orders of magnitude at process pressure and temperature. This required multiple evaporation sources, maintained at different temperatures and located in precise geometric relationships. This process has enabled us to deposit microcolumnar films of CsI:Tl, Sm with thicknesses ranging from 100 to 200 μm , with good control of column morphology. A typical micrograph is presented in Fig. 1, which shows a side view of a 185 μm film with a dense array of well-separated and relatively uniform microcolumns. Depending on the specific conditions of deposition, the columns may be either amorphous or polycrystalline in nature, although the former can be converted into the latter by subsequent annealing under appropriate conditions. We also find that while the concentrations of the respective dopants are quite uniform across the areas of the films, there is generally a gradient along the length of the columns themselves, which can be altered by subsequent thermal treatment. The significance of this upon both the scintillation and imaging properties remains to be determined, and further study in this area is currently under way.

III. Imaging Performance

Prior to performance evaluation, the deposited films were first coated with a thin layer of optically clear protective material having a low refractive index, providing both moisture and mechanical protection. For X-ray imaging the microcolumnar CsI:Tl was pressure-coupled to the CCD fiberoptic window.

The imaging performance of the system was evaluated in terms of the modulation transfer function (MTF) and detective quantum efficiency (DQE). The X-ray source used for these measurements was a GE Senographe 600T-FD with a molybdenum (Mo) target, with Mo filtration and a focal spot of 300 μm . Power was provided by a 22–36 kVp pulsed variable energy source operated at 28 kVp, and the source-to-detector distance was maintained at 65 cm. During each measurement the exposure was monitored using a Radcal Corporation equipped with a model 9015 air ionization chamber and the data were corrected for any variations in exposure.

Data was acquired by pressure-coupling the screen of interest to a high-resolution CCD camera. To measure the resolution in terms of contrast transfer function (CTF(f)), images of a standard line pair phantom were acquired and the line profile through the line pair phantom was used to demonstrate the modulation at various spatial frequencies. To evaluate spatial resolution of the screen, the pre-sampling MTF was measured according to the technique described by Fujita *et al.* [13] and others [14]–[16]. From the measured pre-sampling MTF, the $\text{NPS}_{\text{normalized}}(f, \varphi_x)$ and the photon fluence/exposure (φ_x) of the incident X-ray spectrum, the DQE(f) of the imaging system was calculated as

$$\text{DQE}(f) = \frac{\text{MTF}^2(f)}{\varphi_x \cdot \text{NPS}_{\text{normalized}}(f, \varphi_x)}.$$

Procedures to measure these quantities are also outlined by Roehrig *et al.* [17]. We performed such measurements on codoped CsI:Tl, Sm screens 185 μm thick, and compared the results with those from a regular CsI:Tl film and a Min-R 2000 GOS screen with thickness giving about the same stopping power for the exciting radiation.

The first comparison deals with light output. As seen in Table I, our new codoped CsI:Tl, Sm microcolumnar film yields more than twice as much light at the same level of excitation as does the commercial Min-R product at thicknesses providing equivalent stopping power, and significantly outperforms standard CsI:Tl films as well. This demonstrates that, contrary to earlier concerns, the presence of the codoping additive need not diminish the light output of CsI:Tl, but rather, at appropriate concentrations, may actually enhance it.

The spatial resolution of these films was evaluated by measuring the presampling MTF as a function of the spatial frequency. These measurements were performed using a 10 μm slit and 28 kVp X-rays, and the results are presented in Fig. 2. Here it is clearly evident that even at a thickness of 185 μm , the new codoped CsI:Tl, Sm microcolumnar film resolves to a spatial frequency greater than 10 lp/mm with an amplitude greater than 10%, an excellent performance with at least twice the amplitude provided by commercial high-resolution CsI:Tl films at that point. This is even better than Min-R at the same spatial frequency, despite the fact that the latter is some 40% thinner. And it is clearly superior to the (25% thinner) Lanex R (GOS) screen, which resolves only 4 lp/mm at 10% modulation.

We also examined the effect of the Sm codopant upon the DQE of CsI:Tl microcolumnar films; these results are presented in Fig. 3. Note that at a frequency value of zero, the DQE of both screens is essentially the same (~65%); this is as expected, since it is largely determined by the X-ray absorption efficiency of the host material (CsI), where the dopants are not present in a high enough concentration for any substantive effect. Indeed the slightly lower value for the codoped material is fully consistent with its slightly lower thickness. But the far more significant observation is at the higher spatial frequencies, where the DQE of codoped CsI:Tl, Sm is extraordinarily high. This reflects the rapidly growing ratio between

the MTF values of the two materials with increasing spatial frequency, which can be attributed to the improved, well-separated, microcolumnar structure.

IV. Afterglow and Hysteresis

For rapid sequential image acquisition, such as in CT applications, afterglow and hysteresis are important considerations. But as we already know, neither of these is a well-defined material property, but strongly dependent on the excitation conditions. This is clearly illustrated in Fig. 4, which compares the afterglow from microcolumnar films of CsI:Tl, with and without the Sm^{2+} codopant, after excitation by X-ray pulses of widely different duration. Here we see that after short pulse (20 ns) excitation, the residual signal 20 ms later is quite low (some seven orders of magnitude below the peak) whether or not the Sm^{2+} codopant is present. As in the codoped single crystal, Sm^{2+} does provide some suppressive effect (a bit more than a factor of two), but this is less than had been observed in single crystals, a difference that may be attributed to the higher incidence of lattice defects inherent in the nonequilibrium vapor deposition process.

But as the excitation pulse widens, the picture changes dramatically. As we see in the figure, the afterglow (as a fraction of the luminescence intensity during excitation) becomes more and more pronounced, so that for a pulse that lasts 100 ms the emission that persists immediately after cessation can be more than 5% of what it was during the excitation pulse itself. But the suppressive effect of the Sm^{2+} additive grows stronger yet, now reducing the afterglow by almost an order of magnitude compared to conventional CsI:Tl microcolumnar films. And, since (as we have already seen in single crystals [10], [11]) Sm^{2+} provides a nonradiative relaxation path to drain the trapped carriers that would otherwise have generated afterglow, it maintains its beneficial effects as long as many seconds after the pulse has ended.

V. Fast Imaging

To demonstrate the effects of scintillator persistence (afterglow) in fast imaging applications, we coupled a $185\text{ }\mu\text{m}$ microcolumnar CsI:Tl, Sm screen to an EMCCD camera, and acquired a sequence of images showing single γ -ray events from a ^{57}Co source. The EMCCD was operated at 30 fps with 4×4 binning. The results of such measurements are illustrated in Fig. 5.

Here we see two successive frames from the sequence. The excellent resolution of the spots, the high contrast, and the total absence of ghosts from the previous frame provide striking testimony of the superb rapid imaging capabilities of the microcolumnar CsI:Tl, Sm films.

VI. Conclusion

We have found that the major afterglow-suppressive influence exhibited by Sm^{2+} as a codopant in melt-grown CsI:Tl crystals is also significantly effective in vapor-deposited microcolumnar films as well. Techniques have been developed to allow controlled insertion of the codopant into the CsI lattice during the deposition process, despite the wide disparity in the vapor pressures of the three constituents. While the magnitude and temporal characteristics of the suppressive effect are not identical to those in the single crystal, these are matters of fine detail rather than fundamental differences.

The superior scintillation performance of CsI:Tl, Sm has been attributed to the introduction, by the codopant, of a nonradiative recombination mechanism that allows the emptying of traps without the delayed emission. This has already been established in single crystals, and the microcolumnar films appear to be fully consistent with the mathematical model.

We have also characterized the imaging performance of the films in terms of numerical criteria (MTF, DQE), and have also applied them under rapid acquisition conditions. We find them to be superior in all respects to the corresponding results for currently available materials, making them useful for a wide range of multiframe applications, including dynamic radiography, radionuclide imaging, and CT imaging.

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Fig. 1. SEM micrograph of a 185 μm thick microcolumnar film of CsI:Tl, Sm developed at RMD. Upper figure shows top surface, with well-separated columns clearly evident. Lower figure is a cross-section of film-substrate interface, which shows that the film grew as separate columns right from the start, which explains the superb resolution performance.

Fig. 2. Modulation Transfer Function (MTF) of CsI:Tl, Sm microcolumnar films, 185 μm thick, compared with other materials. Note superior performance even to thinner conventional materials, especially at the higher spatial frequencies.

Fig. 3. Detective Quantum Efficiency (DQE) of CsI:Tl, Sm microcolumnar films, 185 μm thick, compared with 200 μm conventional CsI:Tl. Note that while the low frequency values (dominated by stopping power) are essentially the same, the higher frequency values for the codoped material are substantially greater, reflecting the higher MTF at those frequencies.

Fig. 4.

Decay of scintillation light from CsI:Tl microcolumnar films with and without Sm²⁺ afterglow-suppressing additive. Upper graph shows behavior after 20 ns pulse, lower graph after 100 ms square pulse. Note that wide pulse gives greater afterglow, but also greater suppressive effect.

Fig. 5.

Two successive frames from a sequence of images showing single γ -ray events from a ^{57}Co source, detected using a $185\ \mu\text{m}$ thick CsI:Tl, Sm microcolumnar film. Note superb resolution and total absence of ghosts.

TABLE I

Light Output of Microcolumnar CsI:Tl, Sm Films

Material	Thickness (μm)	Light Output (Relative to Kodak Min-R 2000 GOS)	Light Output (Relative to CsI:Tl)
CsI:Tl, Sm	185	2.1	1.7
CsTl	175	1.2	1.0
Min-R	110	1.0	0.8