

## Luminescence properties of CsI:Tl crystals codoped with Eu

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In investigating chemical approach for reducing the afterglow from CsI:Tl, we were discovered es that a particularly effective ion for such afterglow suppression is  $\text{Eu}^{2+}$ . We have extensively studied the effect of the Eu codopant on the luminescence from crystals of CsI:Tl. Numerous single crystals of CsI:Tl,Eu were grown by the Bridgman technique in evacuated quartz ampoules at concentrations between 0.05 and 0.5 mole percent. Three different materials were investigated as sources for the codopant: two variants of  $\text{EuI}_2$  and elemental Eu metal. X-ray excited spectra revealed the presence of an additional peak at about 460 nm, characteristic of  $\text{Eu}^{2+}$  ions in the CsI lattice. The decay traces of the specimens reveal substantial variation in afterglow suppression, and possible reasons for these differences are examined and discussed.

Проведено исследование влияния различных легирующих примесей на величину послесвечения CsI:Tl. Достаточный для практического применения эффект уменьшения послесвечения обнаружен при введении примеси  $\text{Eu}^{2+}$ . Монокристаллы CsI:Tl:Eu с содержанием Eu в исходном материале от 0,05 до 0,5 мольных процентов выращены методом Бриджмена в вакуумированных кварцевых ампулах. В качестве легирующей примеси Eu исследован  $\text{EuI}_2$  от двух различных производителей и металлический Eu. Эмиссионные рентгеновские спектры выращенных монокристаллов обнаруживают присутствие дополнительного пика с максимумом около 460 нм, характерного для ионов  $\text{Eu}^{2+}$  в решетке CsI. Кривые затухания образцов с различными источниками ионов показали существенные вариации в эффекте подавления послесвечения. Обсуждаются возможные причины такого различия.

CsI:Tl is one of the most highly desired scintillator materials for medical and industrial applications. It has the highest conversion efficiency of any known scintillator (64,000 photons/MeV), a rapid initial decay (680 ns), an emission in the visible range (540 nm), and cubic structure that allows fabrication into microcolumnar films. It has a relatively high density (4.53 g/cc), high atomic number ( $Z = 54$ ), and is completely transparent to its own emitted light. In view of these excellent properties, along with its low cost and easy availability [1], CsI:Tl has been the material of choice for radiologi-

cal imaging applications [2, 3], X-ray and gamma ray spectroscopy, homeland security applications, and nuclear medicine applications such as intra-operative surgical probes and SPECT.

Despite the obvious advantages of CsI:Tl, however, it suffers from an intrinsic shortcoming that has hindered its use in CT and many other high speed imaging applications: the presence of a persistent afterglow component in its scintillation decay. Although the initial decay has a characteristic time of 680 ns [2], its residual afterglow at 2 ms after excitation cutoff can be as high

as 5 % of the peak value, depending on the intensity and duration of the excitation pulse. This causes signal 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 [2-4]. If the afterglow in CsI:Tl were significantly reduced, the material could be effectively used in such important modalities as medical cone-beam or spiral CT, enabling improved performance with substantial reduction in cost.

Consequently, we have been exploring the feasibility of suppressing this afterglow by chemical means. We have found that by codoping the CsI:Tl with  $\text{Eu}^{2+}$ , the afterglow in the time range of 10  $\mu\text{s}$ –100 ms can be lowered by almost two orders of magnitude [5]. We have conducted an extensive investigation of this unusual effect, and have derived a detailed mathematical model that explains the underlying kinetic processes («Suppression of afterglow in CsI:Tl by codoping with  $\text{Eu}^{2+}$ », I & II, accepted for publication in Nucl. Instr. & Meth., A, 2006). Nevertheless, and despite the insight that this comprehensive effort has provided, some important questions about the phenomenon remain unanswered, particularly with regard to the influence of fabrication technique. It is the purpose of this paper to address these issues.

The CsI:Tl,Eu crystals for this investigation were grown under a number of different conditions. While all the CsI:Tl starting material (containing 0.08 mole percent Tl) was purchased from Amcrys [6], we used a variety of sources for the Eu codopant:  $\text{Eu}_2$  (nominally anhydrous) from both Aldrich [7] and ESPI [8]; and Eu metal from ESPI. The reason for the multiple sources will become evident shortly. The nominal concentration of the codopant in the starting material was in the range of 0.05–0.5 mole percent. The crystals were grown in evacuated quartz ampoules using the vertical Bridgman technique. The resultant boules were 10 mm in diameter and 35 mm long. From these boules, disks were cut at a constant distance of 20 mm from the upper edge of the boule, to prevent any artifacts that might arise from the inevitable concentration gradient along the axis of the boule. Similarly, in all parametric comparisons, the masses of the crystals and the conditions of their growth were maintained the same, so that we are confident that the concentration relationships are internally consistent. All specimens were polished to optical transparency, with a finished thickness of 2.5 mm.

Spectroscopic measurements were performed under steady-state excitation by 8keV Cu  $K\alpha$  X-rays emitted from a Philips diffractometric source operated at 40 kV with 20 mA current. The resulting scintillation light was collected in a McPherson 0.2 m monochromator (model 234/302) that separated the light into its wavelength components, and the intensity of the selected wavelength was registered with an RCA C31034 photomultiplier tube (PMT). The operation of the instrument, including X-ray trigger, the rotation of the monochromator to scan the wavelengths, and data acquisition and analysis was software controlled. The decay patterns of the scintillation emission were measured under both short pulse and extended pulse conditions. For the former, specimens were excited by means of a Golden Engineering XRS-3 source, which provides X-ray pulses 20 ns FWHM with nominal maximum photon energy of 250 kVp. The scintillation response from the specimens was passed through a 0.2 m McPherson monochromator set at 560 nm, detected by a Hamamatsu R2059 photomultiplier, and recorded by a Tektronix TDS220 digital storage oscilloscope. To explore the manner in which the afterglow is affected by the intensity and duration of the initial excitation, we performed similar measurements over a wide range of excitation conditions. For this we set up a special apparatus consisting of a 60 kW Electromed CPX160 X-ray generator with a Varian rotating anode tube (model A292), capable of providing square pulses ranging in length from 1 ms to 8 s, over a similarly wide range of tube voltages and currents. The rise and fall times of the square pulses are specified as about 200  $\mu\text{s}$ , and the scintillation signal is detected by a fast response silicon PIN photodiode made by Hamamatsu, model S3204-8. This instrumentation gives us the capability to measure decay traces under virtually any set of experimental conditions that might be relevant to real applications.

The UV excitation and emission spectra were measured with a dual monochromator system custom-built by McPherson, in which UV excitation from a model 632 deuterium lamp is passed through a model 2035 monochromator, and the resultant emission is analyzed by a model 234/302 monochromator and detected by an RCA C31034 photomultiplier. Excitation spectra were measured with the emission monochromator set to either 460 nm or 550 nm,

while emission spectra were measured with UV excitation wavelengths of 235 nm (short-wave) and 340 nm (long-wave).

The first point we wish to discuss is the after-glow suppression phenomenon, which is, after all, the motivation for the work we are reporting here. For a number of years we have been involved in a comprehensive program [9] to characterize the mechanisms that govern the generation of afterglow in CsI:Tl and to suppress those mechanisms by means of selective incorporation of codopant ions. While most of the effects were modest [10], we have found that one particular ion, namely  $\text{Eu}^{2+}$ , exerts an afterglow-suppressive effect at least an order of magnitude greater than any of the others (Fig. 1). Indeed, at 1 ms after the excitation pulse, the presence of  $\text{Eu}^{2+}$  reduces the afterglow by a factor of 30. In extensive studies of this phenomenon [9], performed largely on crystals whose codopant was provided by the ESPI source material, we were able to fully characterize the effect and to define the material composition that would provide optimal scintillation behavior. These studies also found that the afterglow, expressed as a fraction of the intensity observed before excitation cut-off, was a strong function of the duration of the excitation pulse.

Perhaps the most significant outcome of this program was the understanding it provided on the entire scintillation process. With the aid of thermoluminescence measurements we developed a phenomenological model for afterglow suppression in codoped CsI:Tl, Eu. This model indicates that trapping of holes to form stable  $V_{KA}(\text{Tl}^+)$  centers is common to CsI:Tl both with and without  $\text{Eu}^{2+}$ , and plays a major role in the afterglow. Codoping of CsI:Tl with  $\text{Eu}^{2+}$  introduces deep electron traps, which give rise to new room-temperature glow peaks; these new traps effectively scavenge the electrons from the shallow traps associated with thallium, thus suppressing afterglow in the time domain of tens of milliseconds. The measurements supply input for rate equations, which provide an excellent simulation to the experimentally observed behavior of the afterglow. Unfortunately this leads to a kinetic trade-off, since the ultimate release of carriers trapped by the europium contributes to enhanced afterglow in the longer time domain of seconds and minutes. The model further says that during excitation most of the energy is transported to activators by excitons that bypass both electron and hole traps. Consequently, the scintilla-

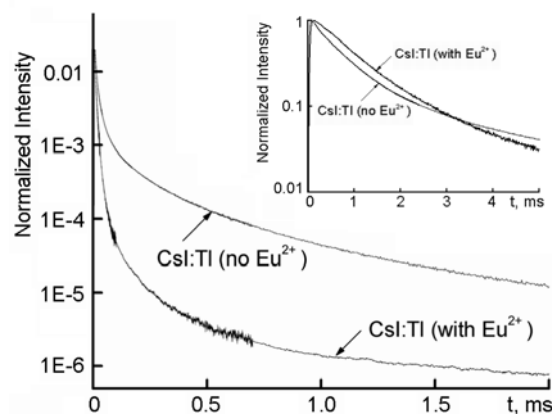


Fig. 1. Standard semilog plot of the scintillation decay of CsI:Tl after short-pulse ( $\sim 20$  ns) excitation, with and without  $\text{Eu}^{2+}$  as decay-modifying additive. At 1 ms after the pulse,  $\text{Eu}^{2+}$  suppresses the afterglow by about a factor of 30. Inset shows detail of the first 5  $\mu\text{s}$ .

tion light output remains virtually constant during excitation regardless of its duration, even though the traps are far from saturated. For the same reason, the long-time afterglow is predicted to be proportional to the duration of the excitation but nearly independent of its intensity, as is indeed observed. The details of the modeling effort are discussed elsewhere [10].

Given that the afterglow-suppressive effect of  $\text{Eu}^{2+}$  in CsI:Tl depends on the complex interplay of various trapping processes, it should not be surprising to find the effect to be dependent on both the conditions of crystal growth and the chemical nature of Eu source. As indicated in the Experimental section, in this work we investigated three different source materials:  $\text{EuI}_2$  anhydrous 99.9 % elemental purity from Aldrich;  $\text{EuI}_2$  anhydrous (99.99 %) from ESPI; and Eu metal (99.99 %) from ESPI. We found that both the kinetic and spectroscopic behavior of the codoped crystals were exquisitely sensitive to the choice among these three sources for introducing the desired codopant. The salient points are summarized below.

The first point we address is the physical appearance of the crystal boules. Here we find a remarkable variation depending on the source of dopant material. With  $\text{EuI}_2$  from Aldrich, we invariably obtained boules that were pale green in color. In contrast, when the  $\text{EuI}_2$  source was ESPI, the crystals were pale pinkish yellow, with those containing the highest Eu concentration (0.5 mole%) also displaying a pronounced

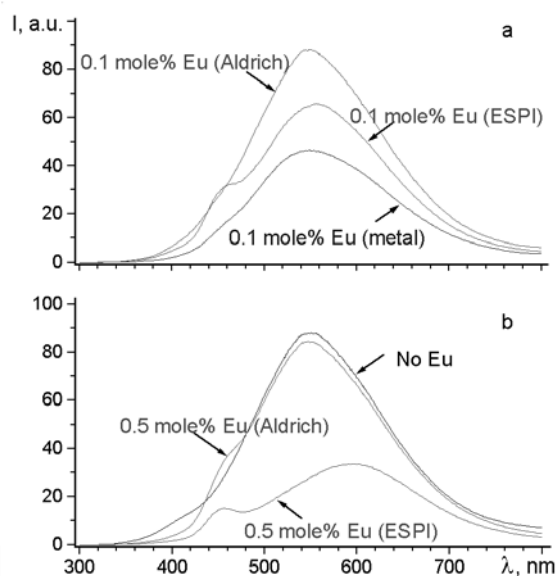


Fig. 2. Spectra of X-ray excited emission from CsI:Tl,Eu specimens at two different concentrations of codopant from various sources.

dark red deposit on the surface, resembling elemental iodine. With metallic europium as the codopant source, the boules took on yet a third appearance, with little evident body color.

The differences in specimen appearance were accompanied by corresponding differences in the spectra of the X-ray-excited scintillation. As seen in Fig. 2, CsI:Tl without codopant yields the familiar broad quasi-Lorentzian band centered in the yellow-green and spanning the entire visible region of the spectrum. With  $\text{EuI}_2$  from ESPI, we see two major changes: a distinct shift of the  $\text{Tl}^+$  emission to the red, and a new satellite peak at about 460 nm, both of which become more pronounced with greater Eu concentration. The same satellite peak is found when the Aldrich material provides the codopant, but it is less well resolved, and the main ( $\text{Tl}^+$ ) peak hardly shifts at all. Finally, when europium metal is the codopant source, the satellite corresponding to the  $\text{Eu}^{2+}$  emission subsides to a small shoulder on the left side of the broad  $\text{Tl}^+$  emission. As in the previous case, the primary  $\text{Tl}^+$  band is virtually identical in both shape and location to what we get from standard CsI:Tl without codopant. Indeed, the two peaks appear to be simple superpositions of two independent emissions, with no interaction whatever.

More distinctive behavior is found when the emission is excited by long-UV (340 nm)

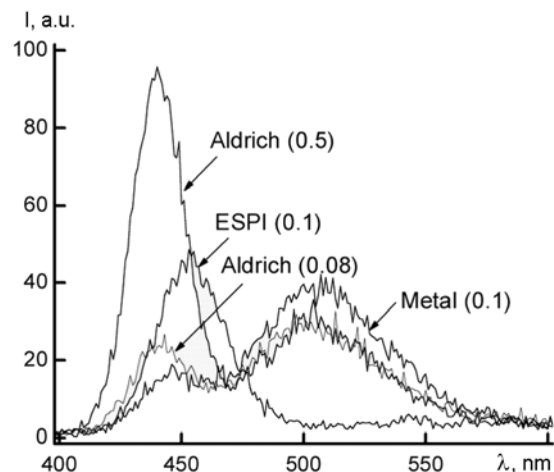


Fig. 3. Emission spectra of CsI:Tl,Eu specimens prepared from various sources of codopant, excited by continuous UV irradiation at 340 nm. Spectrum of uncoded CsI:Tl is shown as reference.

rather than by X-ray. Under these conditions only the blue  $\text{Eu}^{2+}$  emission at about 450 nm is seen in the ESPI-derived material (Fig. 3), with virtually none of the broad green  $\text{Tl}^+$  band so prominent in the scintillation (Fig. 2). This is as expected, since excitation of the latter requires higher energy than is available in long UV photons. The other two materials, however, show two distinct peaks, one in the green centered at about 500 nm and one in the blue with a maximum at about 440 nm. While the latter (which becomes stronger with higher concentrations of the codopant) is almost surely the expected emission from individual  $\text{Eu}^{2+}$  sites, the origin of the green peak is uncertain. This emission has previously been reported in cesium halides by other investigators, and has been attributed to the formation of either aggregate centers containing two or more  $\text{Eu}^{2+}$  ions and their associated charge-compensating vacancies [11], or of nanodomains having localized quasi-perovskite ( $\text{CsEuI}_3$  or  $\text{Cs}_4\text{EuI}_6$ ) structure [12]. Energy transfer from  $\text{Eu}^{2+}$  to  $\text{Tl}^+$  is pretty much ruled out by the low concentrations of the two dopants, as well as by the wavelength and shape of the green peak.

The distinctiveness of the ESPI-derived material is most evident in its decay kinetics, when excited by both short and long X-ray pulses. The difference is most pronounced in the 20 ns pulse data, which shows that while all three materials display some degree of afterglow suppression (Fig. 4), the effect is substantial only in the samples

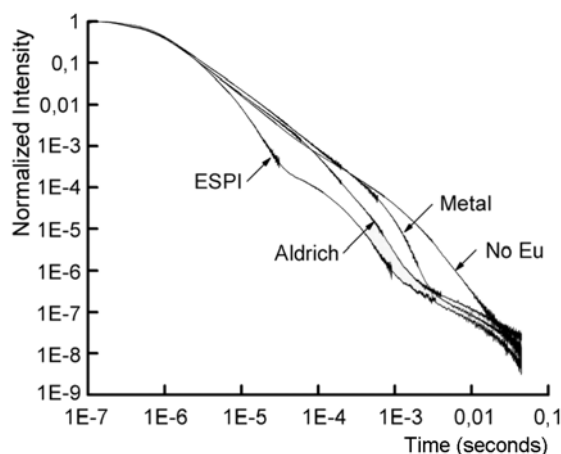


Fig. 4. Log-log plots of the measured scintillation decay after short-pulse (20 ns) X-ray excitation, for CsI:Tl,Eu samples prepared from various sources of codopant. Here and in Fig. 5, the decay of uncodedoped CsI:Tl without codopant is shown as reference.

made from ESPI  $\text{EuI}_2$ . Moreover, the same pattern holds true under long-pulse excitation (Fig. 5) as well. Since it is precisely the afterglow suppression phenomenon that is at the heart of our research program, our motivation for elucidating the described differences in behavior can hardly be overstated.

But what actual chemical differences in the codoping are responsible for the observed disparities in behavior? The most logical hypothesis is some sort of contamination, particularly in the ESPI source material. Here we have two primary suspects, moisture and oxidation, which would have rather different consequences. Let us examine these in turn.

With regard to moisture, the hygroscopic nature of rare earth halides as a class is well known. Moreover, the resultant water of deliquescence is notoriously difficult to remove, generally preferring to react with the host material to liberate the corresponding hydrogen halide gas and depositing hydroxyl ions into the host lattice. This would have serious consequences for the scintillation, since  $\text{OH}^-$  is a very potent quencher of luminescence, through rapid (nanosecond-scale) multiphonon processes. This should result in a pronounced increase in the decay rate of the  $\text{Tl}^+$  emission. But here we see no evidence of such quenching; on the contrary, as illustrated in Fig. 1, the initial decay rate is actually slower in the presence of the Eu additive than without it. Consequently we can largely disregard moisture

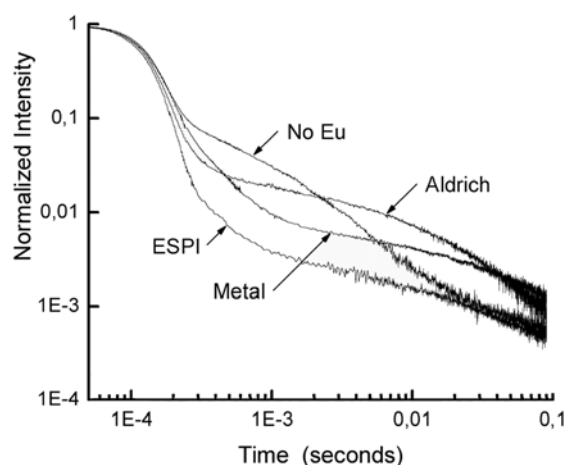


Fig. 5. Log-log plots of the measured scintillation decay after excitation by 100 ns X-ray pulses, for CsI:Tl,Eu specimens prepared from various sources of codopant. The decays cannot be measured at times shorter than 0.2 ms because they are masked by the decay of the excitation pulse.

as a major agent in the afterglow suppression.

In this regard, oxidation is a much more serious issue. Europium is one of only three rare earths that form stable compounds (mostly halides) in the divalent state. But these are extremely vulnerable to oxidation. Thus, if exposed to any traces of ambient air,  $\text{EuI}_2$  will rapidly react to form the oxyiodide and elemental iodine:

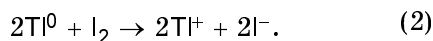


But the CsI lattice is made up of only singly charged ions, and will not accept europium in the tripositive state; instead, it is energetically much more favorable to force reduction of the europium back down to the 2+ state, with the liberation of more elemental iodine. Even so, the dipositive cation still introduces a charge imbalance into the CsI:Tl lattice, which must be compensated in some manner so as to preserve electrical neutrality. In this case, the  $\text{O}^{2-}$  would remain in the lattice, to help provide the necessary balance.

But since it originated from a contaminant, there would not be enough  $\text{O}^{2-}$  to compensate the excess charge from the rest of the  $\text{Eu}^{2+}$ . For this, there are three other possibilities: insertion of an interstitial  $\text{I}^-$  anion; removal of a  $\text{Cs}^+$  cation; or reduction of  $\text{Tl}^+$  to the neutral state. Given the huge ionic radius of  $\text{I}^-$  (2.2 Å) and the high packing density of the lattice, we can effectively disregard the first option, leaving only the

cation vacancy and  $Tl^+$  reduction for further consideration. And since both are known to occur in the  $CsI:Tl$  lattice, the issue becomes essentially one of relative proportions.

We believe that the manner in which the charge balance is achieved is the key to the puzzle. If the ESPI  $EuI_2$  were indeed contaminated slightly by  $Eu^{3+}$ , the consequent generation of elemental iodine would tend to suppress formation of  $Tl^0$ :



This would force charge compensation to occur largely by  $Cs^+$  vacancies. The diminished content of  $Tl^0$  would alter the decay kinetics, while the increased abundance of cation vacancies would alter the crystal field at the  $Tl^+$  emitting centers, shifting and reshaping the spectrum of the emission. We have already observed both of these effects.

Here we find additional supporting observations. We have already remarked on the dark red deposit at the surface of the boule, seen at  $Eu$  concentrations of 0.2 mole% or higher, which we took as an indication of free elemental iodine in the ampoule. Moreover, in experiments on polycrystalline codoped material (formed by rapidly quenching the melt), we also observed the characteristic purplish color of  $I_2$  vapor in the sealed ampoule in the space above the melt. Thus we feel that we are on the right track.

The specimens derived from the Aldrich  $EuI_2$  also fit nicely into the hypothetical model. In these specimens, the absence of free elemental iodine allows  $Tl^0$  to play a significant role in compensating the excess cationic charge provided by  $Eu^{2+}$ , reducing the abundance of cation vacancies and their damaging influence on lattice periodicity and hence the crystal field at the emitting sites. And, since the greater abundance of  $Tl^0$  species necessarily provides a large reservoir of electrons trapped at  $Tl$  sites, the kinetic effect of the competing electron traps introduced by the  $Eu$  would be correspondingly diluted.

The specimens derived from elemental metallic  $Eu$  extend the spectroscopic and kinetic trends displayed by the crystals grown using Aldrich  $EuI_2$ , as already described. Here we have a complicating factor in that the metal must somehow be raised to the 2+ state in order to enter the  $CsI$  lattice. This complication is more apparent than real, however, since  $Eu$  metal is one of the

strongest reducing agents known, readily capable of reducing not only  $Tl^+$ , but even the  $Cs^+$  cation as well [13]. Thus its effect would be the exact opposite of the elemental iodine described earlier, enhancing the abundance of the  $Tl^0$  species and exacerbating the trends displayed by the Aldrich-derived material.

Our hypothetical model also provides a recipe for maximizing the desired afterglow-suppressing effect. It predicts that the simple expedient of adding elemental iodine to the starting material should allow the desired performance to be achieved regardless of the origin of the codopant. While the requisite experiments have not yet been completed, preliminary results do indeed appear to confirm the predictions of the model. Thus it appears that in every respect our hypothetical model is fully consistent with reality.

In conclusion, we have found that the afterglow exhibited by  $CsI:Tl$  can be substantially reduced by the addition of  $Eu^{2+}$  as a codopant. The suppressive effect is most pronounced in the time scale between 0.2 and 20 milliseconds after cutoff of excitation, and is strongly dependent on the duration of the excitation pulse. The codopant provides deep electron traps to divert free electrons that would otherwise recombine at  $Tl$  emitting centers, delaying their emission and redistributing it over a longer time scale.

The phenomenon, however, was found to be surprisingly sensitive to the source material used to provide the codopant, and a hypothetical model was created to explain the experimental observations. The suppressive phenomenon turned out not to be an intrinsic property of the codopant, but to depend strongly on the conditions of its insertion into the lattice. The most important of these is that crystal growth should be performed in the presence of elemental iodine, so as to suppress formation of  $Tl^0$ . Thus the work reported here resolves a major problem in controlling the afterglow from  $CsI:Tl$ , enabling this material to be utilized in rapid imaging applications.

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## Люмінесцентні властивості кристалів CsI:Tl, активованих Eu

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Проведено дослідження впливу різних легуючих домішок на величину післясвітіння Cs:Tl. Достатній для практичного застосування ефект зменшення післясвітіння виявлений при введенні домішки Eu<sup>2+</sup>. Монокристали Cs:Tl:Eu і вмістом Eu у вихідному матеріалі від 0,05 до 0,5 мольних відсотків вирощені методом Бриджмена у вакуумованих кварцевих ампулах. Як легуюча домішка Eu досліджений Eu<sub>2</sub> від двох різних виробників і металевий Eu. Емісійні рентгенівські спектри вирощених монокристалів виявляють присутність додаткового піка з максимумом близько 460 нм, характерного для іонів Eu<sup>2+</sup> у ґратці Cs. Криві загасання зразків з різними джерелами іонів показали істотні варіації в ефекті придушення післясвітіння. Обговорюються можливі причини такого розходження.