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Simultaneous improvement in afterglow, light yield and energy resolution in CsI:Tl-based scintillators paves the way to its application in computer tomography and high-speed imaging.
CsI:Tl\textsuperscript{+},Yb\textsuperscript{2+}:Ultra-high light yield scintillator with reduced afterglow

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Afterglow problem has been preventing CsI:Tl single crystal scintillators from applications in the field of computer tomography and high-speed imaging. We show that Yb\textsuperscript{2+} codoping in CsI:Tl can reduce it at least by one order of magnitude after 50 ms from X-ray cut-off compared to ordinary CsI:Tl. After optimization of the Yb\textsuperscript{2+} and Tl\textsuperscript{+} concentrations, the doubly doped CsI:Tl,Yb crystal exhibits an ultra-high light yield of 90,000±6000 photons/MeV, energy resolution 7.9% at 511 keV and low afterglow level of about 0.035% at 80 ms. Simultaneous improvement in afterglow, light yield and energy resolution in CsI:Tl-based scintillators paves the way to its application in computer tomography and high-speed imaging. The physical mechanism and role of ytterbium ions in afterglow suppression were proposed.

Tl-doped cesium iodide was introduced in 1951 as one of the first single crystal scintillators.\textsuperscript{1} It shows high light yield 66,000 photons/MeV, scintillation response dominated by 800-1000 ns decay time and an emission band at 550 nm matching well the semiconductor photodetector sensitivity range.\textsuperscript{2} Furthermore, it has medium density (4.53 g/cm\textsuperscript{3}) and higher effective atomic number (Z\text{eff} = 54) and allows the fabrication of micro-columnar films. Given its low cost, CsI:Tl materials became widely used for radiological imaging,\textsuperscript{3} x-ray and gamma ray spectroscopy, homeland security and nuclear medicine applications. However, due to the persistent afterglow in CsI:Tl attributed to thermal ionization of trapped electrons (Tl\textsubscript{b}) followed by radiative recombination with trapped holes [V\textsubscript{K}\textsubscript{A} (Tl\textsuperscript{+})],\textsuperscript{4} which causes the pulse pileup in high count-rate applications, its usage in computer tomography (CT) and high-speed imaging applications is disabled.\textsuperscript{5,6} Thus, the way to suppress the afterglow in CsI:Tl has been searched intensively in last two decades.

In general, codoping by an appropriate ion was found an effective method to suppress the afterglow in scintillators and phosphors as has been shown e.g. in Gd\textsubscript{2}O\textsubscript{2}S-based or (Y,Gd)\textsubscript{2}O\textsubscript{3}-based phosphors and optical ceramics, see Ref. 2 and refs. therein. Afterglow in Lu\textsubscript{2}SiO\textsubscript{5}:Ce (LSO:Ce) scintillator has been soon recognized as a serious limitation\textsuperscript{7} and the Ca\textsuperscript{2+} codoping was found efficient for its suppression.\textsuperscript{8,9} Positive role of Yb\textsuperscript{2+} ions in the afterglow suppression of LSO:Ce was found as well, decreasing it by more than two orders of magnitude, however, at serious expense of the light output.\textsuperscript{10} In CsI:Tl scintillators, the afterglow level was effectively reduced by codoping Eu\textsuperscript{2+} and Sm\textsuperscript{2+} ions.\textsuperscript{11-14} Nevertheless, the atomistic mechanism of Eu\textsuperscript{2+} and Sm\textsuperscript{2+} functioning is utterly different. Samarium ions introduce a non-radiative recombination channel that decreases the radiative recombination of trapped carriers,\textsuperscript{14} but co-doping with europium introduces deep electron traps scavenging electrons from shallow traps associated with thallium, which results in a slower afterglow.\textsuperscript{12} However, co-doping with these ions seriously deteriorated the light yield in both cases. Recently, Totsuka et al. claimed that using the Bi\textsuperscript{3+} codoping the afterglow of CsI:Tl can be less than 0.1% after 10 ms without strong decrease of the radioluminescence efficiency under low energy X-ray (less than 30 keV) excitation.\textsuperscript{13} However, in the attempt to verify this result, we found that the light yield and energy resolution of Bi-codoped CsI:Tl crystals became much worse even for the lowest Bi concentration of about 0.005 mol% (in the melt).\textsuperscript{16}

Therefore, despite of the success in the afterglow suppression in CsI:Tl the codoping strategies mentioned above have simultaneously deteriorated the other important scintillation characteristics such as light yield and energy resolution which points to the complex character of scintillation mechanism. Impurities (doped ions) may introduce energy levels in the band gap of the host crystal which interfere with the charge carrier migration and relaxation processes: while the afterglow level is dramatically improved, other scintillation properties such as light yield and energy resolution may be seriously degraded.

The search for codopants which can effectively diminish the delayed radiative recombination (afterglow) at Tl\textsuperscript{+} centres and not deleteriously affect other scintillation properties is the primary goal of this work. Due to the electronic structure similarity between Eu\textsuperscript{2+} and Yb\textsuperscript{2+}, the afterglow suppression effect by Yb\textsuperscript{2+} codoping is expected. Thus, in this paper, we study the effects of Yb\textsuperscript{2+} co-doping on the optical and scintillation properties of CsI:Tl, including afterglow level, light yield, energy resolution, and relative scintillation efficiency.

We used vertical Bridgman technique to grow two groups of CsI:Tl,Yb crystals. The crystals referred to as group A are used for screening the effect of Yb\textsuperscript{2+} codoping: CsI:0.078mol%Tl\textsuperscript{+} (further denoted as IT1), CsI:0.078mol%Tl\textsuperscript{+}0.005mol%Yb\textsuperscript{2+} (further denoted as IT2) and CsI:0.078mol%Tl\textsuperscript{+}0.05mol%Yb\textsuperscript{2+} (further denoted as IT3). The other crystals referred to as group B are to further optimize the recipe: CsI:0.156mol%Tl\textsuperscript{+} (further denoted as ST3), CsI:0.156mol%Tl\textsuperscript{+}0.005mol%Yb\textsuperscript{2+} (further denoted as ST4) and CsI:0.156mol%Tl\textsuperscript{+}0.05mol%Yb\textsuperscript{2+} (further denoted as ST5).
denoted as ST1) and CsI:0.234mol%Tl+,0.005mol%Yb2+ (further denoted as ST4). The high-purity CsI (5N), TlI (4N) (both from Chemetall), and YbI2 (5N) (Aldrich) according to the stoichiometric ratio were loaded in the quartz ampoules and then heated in vacuum to eliminate the residual humidity. The ampoules were maintained at a temperature 100°C above the melting point of cesium iodide for 24 hours to ensure homogeneity of the melt. Then, ampoules were passed through an optimal temperature gradient with a speed of 0.6 mm/h. The resultant boules were 35 mm in diameter and 100 mm in length. All the crystals were transparent and colorless (see inset of Figure 1). The samples used for dopant concentration measurement were cut at the same position along the boule. The actual dopant concentrations in the crystals were measured by Perkin-Elmer ELAN DRC-e Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The measured Ti⁺ concentration in crystals are listed in Table 1 and Table 2. Yb concentration was below sensitivity limit of the apparatus (5 ppm) so that the data are not shown here. All samples were clear and uniform, without any visible inclusions or cracks. Two sample dimensions were chosen for measurements. The first one was 25.4×25.4 mm² double-faced polished crystals (see inset of Figure 1). These samples were wrapped in Teflon tapes and used for afterglow, pulse height spectra and X-ray excited luminescence spectra measurements. Before these measurements, all wrapped crystals were stored in the dark for at least 24 hrs. The second sample dimension was double-faced polished 5×5×2 mm³ plate used for the rest of measurements.

The afterglow curves were measured by using a single-shot pulse X-ray excitation (pulse duration of 80 ns). The afterglow profiles were recorded by using 20000 data points taken from the oscilloscope (Tektronix DPO 5104) using a photomultiplier (PMT) tube detection (R669). The afterglow level η(t) was calculated as a ratio between the luminescence intensities (I₀ measured during the X-ray irradiation pulse and at the time delay t) after the irradiation is terminated, namely η(t) = I(t)/I₀ × 100%. The wrapped cylinder group A crystals for light yield measurement were coupled with a Hamamatsu R878-WT1734 series PMT with no optical grease or other coupling material. The crystals were excited with 662 keV gamma rays from ¹³⁷Cs source located 10 mm from the crystal surface, and then pulse-height spectra were recorded by Digibase multichannel spectrometer. The shaping time and PMT high voltage was fixed at 2 μs and 1050 V, respectively. The natural background spectrum from the crystal was not subtracted.

The wrapped cylinder group B crystals for absolute light yield and energy resolution measurements were coupled with a Hamamatsu R1306 PMT with a bi-alkali photo-cathode and a borosilicate glass window. A collimated ²²Na source (511keV) was used to excite the samples. The photopake positions were obtained by a simple Gaussian fit. The light output (LO) is measured by single photo-electron peak calibration. The absolute light yield (LY) was calculated using LO, the emission weighted quantum efficiency (EWQE) of the Hamamatsu R1306 PMT at 550 nm which is of about 5±0.5%, and light collection efficiency (LCE) which is assumed to be 1. The specific equation LY [photons/MeV] = LO [photoelectrons/MeV] / (EWQE × LCE) was used. Scintillation decay time was measured by the same equipment by tuning the integration time. Scintillation measurements described for group B samples were performed at Prof. Renyuan Zhu’s HEP group in California Institute of Technology.

The radioluminescence spectra without calibration were conducted on an X-ray Excited Luminescence Spectrometer, assembled at Shanghai Institute of Ceramics. The excitation source of this equipment is medical F30III-2 type mobile diagnostic X-ray machine coupled with 44W plane grating monochromator and Hamamatsu R456 PMT. Optical absorption spectra were recorded on a Varian Cary 5000 spectrophotometer. Photoluminescence decay profiles were recorded on Edinburgh FLS920 fluorescence spectrometer, respectively. All the above described measurements were performed at room temperature.

Figure 1 presents the results of afterglow measurements performed at the group A crystals. The afterglow level of the Yb2+ codoped ones decreases by more than one order of magnitude in comparison with Yb2+-free one after 50 ms. Comparing with the Eu2+, Sm2+ or Bi3+ codopants mentioned above the performance of Yb2+ codopant is comparable as it lowers the afterglow level down to 0.041% in comparison with 0.03% for Bi3+, −0.03% for Eu2+ codopant, and −0.1% for Sm2+.13

![Fig. 1 Afterglow profiles of CsI:Tl, Yb2+ group A crystals after X-ray pulse excitation. Inset shows the photograph of double-faced polished group A crystals with different Yb2+ concentration: none (a), 0.005% (b), 0.05% (c).](image)

The emission spectra under steady-state X-ray excitation of group A crystals were measured (see supplemental data). In the Yb-doped samples the emission spectrum exhibits similar pattern to that of the Yb-free one.11 After normalization, an interesting phenomenon was noticed: a gradual decrease of relative intensity to that of the Yb-free one. Afterglow, it means that the Yb2+ codoping is reducing the unwanted slower components. For CsI:Tl, the unwanted slower components (afterglow emission) was ascribed to the delayed Tl-related band
peaking at about 560 nm\(^{18}\) and 400 nm\(^{19}\). Due to the strong decrease of the quantum efficiency of the PMT above 500 nm, the true maximum of the emission at 550-560 nm cannot be observed in our uncorrected spectra. In our spectra, the maximum of this emission in our spectra peaks at 500 nm. The cause for the relative decrease of 400 nm shoulder in the emission spectra of Yb-codoped samples will be discussed in the following paragraph. The photoluminescence decay times of CsI:Tl\(^{2+}\),Yb\(^{3+}\) crystals are also shown in Table 1. All samples exhibit similar values of about 540 ns, slightly shorter than 585 ns reported in Ref. 20, which proves no negative effects coming from Yb codoping on the Tl\(^{+}\) emission centers themselves. The photpeaks in pulse-height spectra were approximated by a gaussian to evaluate the peak position and to estimate the relative light yield (see supplemental data) of group A crystals. Relative light yield values under the 662 keV gamma excitation from \(^{137}\)Cs are also listed in Table 1. At the lowest Yb co)doping concentration (0.005 mol%), the light yield shows approximately 2% loss compared to Yb-free CsI:Tl. For higher co)doping concentration of 0.05 mole%, the light yield loss is about 14%.

After further optimization of Tl\(^{+}\) and Yb\(^{3+}\) concentration, the composition with excellent scintillation performances has been obtained. Pulse height spectra of optimized group B crystals under \(^{22}\)Na (511 keV) excitation are measured. The light outputs as a function of integration time for group B are shown in Fig. 2. When integration time is 4 \(\mu\)s, the light output for ST3, ST1 and ST4 is 3350, 4241, and 4510 p.e./MeV, respectively. Considering the EWQE of R1306 PMT at 550 nm the emission maximum of CsI:Tl\(^{2+}\),Yb\(^{3+}\) and LCE, it is estimated that the light yield of the best Yb-codoped crystal (ST4) can reach 90,000±6000 photons/MeV. The light yield of ST1 sample is 85,000±5000 photons/MeV, which is still much higher than that of the Yb-free one (ST3) which is 67,000±4800 photons/MeV, close to the typical value 65,000 photons/MeV for CsI:Tl single crystal.\(^{21,22}\)

On the basis of the Bartram-Lempicki model \(L_R=10^6(\beta \times E_p)\),\(^{23}\) the number of photons per unit of absorbed energy (MeV) can be roughly estimated, where \(E_p = 6.2\) eV\(^{24}\) is the bandgap of CsI, the value of \(\beta\) is 1.5-1.8\(^{25}\) for ionic halide compounds. Thus, the theoretical light yield \(L_R\) for CsI:Tl should be within 89,600-107,500 photons/MeV. It is evident that the light yield of the optimized CsI:Tl\(^{2+}\),Yb\(^{3+}\) approaches its theoretical value. The reasons for the light yield improvement are not understood at this stage, and further experimental investigation is currently ongoing. The pulse height spectra of optimized CsI:Tl\(^{2+}\),Yb\(^{3+}\) crystals (group B) under \(^{22}\)Na excitation are presented in Fig. 3. The FWHM energy resolutions obtained for 511 keV \(\gamma\)-rays from the \(^{22}\)Na source are 9.2%, 8.1% and 7.9% for ST3, ST1 and ST4, respectively, plotted in Fig. 3. Besides, its scintillation decay time is about 1.3 \(\mu\)s, close to 1.2 \(\mu\)s of Yb-free one (see Table 2).

Fig. 4 shows the afterglow profiles after the X-ray pulse excitation. It is found that the Yb-doped crystal with highest light yield value exhibits the lowest afterglow level of about 0.035% at 80 ms while the Yb-free sample shows about 1.14% (see Table 2). Thus, simultaneous improvement of afterglow, light yield and energy resolution in the Yb-codoped CsI:Tl scintillator, reported for the first time, will pave the way to its application in the fast imaging techniques. We also note that, except the energy resolution, in the case of identical size the physical and other scintillation performances of slightly hygroscopic CsI:Tl\(^{2+}\),Yb\(^{3+}\) crystals are comparable to those of the ultra-efficient (quite hygroscopic) alkali earth iodide scintillator - SrI\(_2\):Eu\(^{3+}\), see comparison in Table 2.

**Fig. 2** Light output as a function of integration time for CsI:Tl\(^{2+}\),Yb\(^{3+}\) group B crystals.

**Fig. 3** Pulse height spectra of optimized CsI:Tl\(^{2+}\),Yb\(^{3+}\) group B crystals coupled with Hamamatsu R1306 PMT under \(^{22}\)Na excitation. Spectra start at channel no. 354, net photopeak position is marked in the figure, and solid red line is the Gaussian approximation of photopeak. The “net peak” equals the measured peak after subtracting the ADC pedestal signal. The equation, energy resolution (E.R.) = FWHM / Channel of “net peak”, is used to determine the energy resolution.
by Yb codoping, unlike in the case of Bi.

Fig. 5 presents the optical absorption spectra of group B crystals after X-ray pulse excitation. We also recall the relative decrease of 400 nm shoulder in the emission spectra of Yb-codoped samples (Table 1) which can be due to nonradiative energy transfer from the Ti-like 400 nm band towards Yb\(^{2+}\) 4f-5d absorption band or due to the change of the energy barrier for thermally stimulated transition from the 400 nm band towards the other co-existing exciton-like minima on the common adiabatic potential surface of the emission center excited state. The observed changes in the absorption and emission characteristics of Ti\(^{+}\) centers in the Yb-codoped crystals points to the spatial correlation between the Yb\(^{3+}\) and Ti\(^{+}\) centers. In such a case the delayed migrating holes can be inhibited to reach Ti\(^{+}\) being captured at Yb\(^{2+}\) ion in the vicinity. The return of Yb\(^{3+}\) + Ti\(^{+}\) excited ion couple to the ground state can be easily nonradiative taking into account the well-known case of Ce\(^{3+}\) emission quenching in the Ce\(^{4+}\) and Yb\(^{2+}\) pairs e.g. in garnet or oxyorthosilicate materials.

Conclusions
In summary, positive role of Yb\(^{2+}\) codoping in the afterglow suppression in CsI:Tl crystals was found. In the optimized composition, the CsI:Tl\(,\text{Yb}\(^{2+}\) crystal has so far exhibited an ultra-high light yield value of 90,000±6000 photons/MeV, energy resolution 7.9%@511 keV and suppressed afterglow level, light yield and energy resolution in the Yb-coded CsI:Tl scintillator compared to standard CsI:Tl one is considered as a breakthrough in the optimization of the scintillator and paves the way for its application in the X-ray fast imaging applications. The afterglow suppression in CsI:Tl\(,\text{Yb}\(^{2+}\) crystal is explained by spatial correlation of Yb\(^{2+}\) and Ti\(^{+}\) ions where the former can trap the delayed migrating holes and inhibit their radiative recombination with Ti\(^{+}\) counterpart.

Acknowledgement
This work was supported by the National Natural Science Foundation of China (Grant No. 51372256). Partial support of the project of Sino-Czech cooperation funded by MEYS (Czech side), KONTAKT II, no. 12185 is also gratefully acknowledged.

Notes and references
Table 1. Luminescence and scintillation characteristics of Ca:Tb,Yb\textsuperscript{3+} group A crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti concentration (mol%)</th>
<th>Yb concentration (mol%)</th>
<th>PL decay constant (t) (ns)</th>
<th>Relative light yield (\lambda=50) (%)</th>
<th>RL integral intensity (%)</th>
<th>RL relat. intensity at 400 nm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IT1</td>
<td>0.078</td>
<td>0.010</td>
<td>540</td>
<td>0.490</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>IT2</td>
<td>0.078</td>
<td>0.011</td>
<td>525</td>
<td>0.041</td>
<td>98</td>
<td>90</td>
</tr>
<tr>
<td>IT3</td>
<td>0.078</td>
<td>0.012</td>
<td>543</td>
<td>0.041</td>
<td>86</td>
<td>76</td>
</tr>
</tbody>
</table>

\(a\) Monitoring at \(\lambda_{\text{exc}}=322\) nm and \(\lambda_{\text{em}}=520\) nm.

\(b\) Measured from the energy spectra under \(^{137}\)Cs excitation.

\(c\) Measured from the data of X-ray excited luminescence spectra.

\(d\) RL intensity at the spectrum maximum is defined as 100%.

Table 2. Scintillation characteristics comparison between Ca:Tb\textsuperscript{3+},Yb\textsuperscript{3+} (group D) and Sr\textsubscript{2}Eu\textsuperscript{3+} single crystals with the identical size.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti concentration (mol%)</th>
<th>Yb concentration (mol%)</th>
<th>Scintillation decay constant (t) (ns)</th>
<th>Afterglow level (%@50ms)</th>
<th>Light yield @4000eV (photons/MeV)</th>
<th>Energy resolution @511eV (%)</th>
<th>Hygroscopicity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr\textsubscript{2}Eu\textsuperscript{3+}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ca:Tb\textsuperscript{3+} (ST1)</td>
<td>0.156</td>
<td>0.039</td>
<td>1900</td>
<td>3.96</td>
<td>1.450</td>
<td>67000.0±4000</td>
<td>Slight</td>
<td>[26, 27]</td>
</tr>
<tr>
<td>Ca:Tb\textsuperscript{3+},Yb\textsuperscript{3+} (ST1)</td>
<td>0.156</td>
<td>0.031</td>
<td>1164</td>
<td>0.340</td>
<td>0.122</td>
<td>85000.0±5000</td>
<td>Slight</td>
<td>This work</td>
</tr>
<tr>
<td>Ca:Tb\textsuperscript{3+},Yb\textsuperscript{3+} (ST4)</td>
<td>0.234</td>
<td>0.070</td>
<td>1347</td>
<td>0.340</td>
<td>0.035</td>
<td>90000.0±6000</td>
<td>Slight</td>
<td>This work</td>
</tr>
</tbody>
</table>

\(a\) Excited under \(^{60}\)Na with 511 keV.

\(b\) Depend on Eu\textsuperscript{3+} concentration.

\(c\) Excited under \(^{137}\)Cs with 662 keV.