Picosecond Studies of Transient Absorption Induced by BandGap Excitation of CsI and CsI:Tl at Room Temperature

Richard T. Williams, *Member, IEEE*, Kamil B. Ucer, Joel Quedar Grim, Kyle C. Lipke, Larysa M. Trefilova, and William W. Moses, *Member, IEEE*

Abstract—We report picosecond time-resolved measurements of optical absorption induced by a sub-picosecond pulse of light producing two-photon bandgap excitation of CsI and CsI:Tl at room temperature. The transient spectrum of undoped CsI reveals for the first time strong infrared absorption rising through the 0.8-eV limit of present measurements. We suggest that this infrared band is due to transitions of the bound electron in the off-center self-trapped exciton (STE), implying that there should be a band deeper in the infrared associated with the known on-center STE in CsI. Previously reported visible and ultraviolet transient absorption bands at 1.7, 2.5, and 3.4 eV are confirmed in these measurements as attributable to hole excitations of STE. In 0.3% thallium doped CsI, infrared absorption possibly attributable to STEs is observed for approximately the first 5 ps after excitation at room temperature, but decays quickly. The absorption bands of Tl^0 (electron trapped at Tl^+ activator) and of self-trapped holes are the main species seen at longer times after excitation, during which most of a scintillation pulse would occur. This is in accord with a recently published report of nanosecond induced absorption in CsI:Tl.

Index Terms—CsI, scintillators, self-trapped exciton, transient absorption.

I. INTRODUCTION

BOTH pure CsI and thallium-doped CsI:Tl are useful scintillators for radiation detection and γ-spectroscopy. The 4.1-eV scintillation luminescence band in pure CsI at room temperature is generally understood to result from radiative decay of self-trapped excitons (STE) [1]. The 15-ns lifetime of its room-temperature luminescence makes undoped CsI

R. T. Williams, K. B. Ucer, J. Q. Grim and K. C. Lipke are with the Department of Physics, Wake Forest University, Winston-Salem, NC 27109 USA (e-mail: williams@wfu.edu; ucerkb@wfu.edu; grimjq@wfu.edu; lipkkc7@wfu.edu).

L. M. Trefilova is with the Institute for Scintillation Materials, Kharkov 61001, Ukraine (e-mail: shpil@isc.kharkov.com).

W. W. Moses is with Lawrence Berkeley National Laboratory, Berkeley, CA 94720-8119 USA (e-mail: wwmoses@lbl.gov).

useful for fast timing applications. Two spectrally distinct luminescence bands are seen at low temperature at 4.3 and 3.7 eV. Nishimura *et al.* ascribed these bands to on-center and off-center STEs, respectively [1]. The on-center configuration they proposed is the V_k-like di-iodide halogen core with a loosely bound electron, as attributed in works on other alkali halides [2]–[4]. At room temperature, the 4.3- and 3.7-eV luminescence bands have merged or given way to a single broad band at 4.1 eV. Nishimura *et al.* proposed that the room-temperature 4.1-eV luminescence comes from radiative decay of the on-center STE, spectrally shifted from 4.3 eV by occupation of higher vibrational states and populated by thermally activated transfer from the off-center STEs accounting for the 3.7-eV luminescence. The contribution of the equilibrated STEs spending time in the on-center configuration dominates the luminescence spectrum because of the higher radiative transition rate of on-center STEs [3], [4].

In 1998, Gafiatulina *et al.* published the first spectra of transient absorption in undoped CsI over the spectral range 320 to 1130 nm, time range 15–500 ns, and temperature range 80 to 550 K [5]. The absorption was induced by a pulse of 250-keV electrons of duration 10 ns. They found that the main features of induced absorption at room temperature and below could be tied by shared decay time to self-trapped exciton luminescence. They proposed a model of on-center and off-center STE configurations to account for the absorption spectra at room temperature and below. However, some of their band assignments differ significantly from the model of Nishimura *et al.* [1]. The appearance of a 3.4-eV ultraviolet absorption band in the transient spectrum led Gafiatulina *et al.* to suggest a tri-iodide on-center STE as an additional lattice configuration, and this further led them to attribute the 3.7-eV low-temperature luminescence and the 4.1-eV room-temperature luminescence to different STE configurations than those assigned by Nishimura *et al.* Despite differences in details of the assignments, it can be summarized that all three of the visible-uv transient absorption bands seen in [5] can be reasonably attributed to hole transitions on the STE core. However, it is difficult to distinguish on-center or off-center STE configurations just from looking at the broad and fairly unstructured hole excitation bands.

The electron excitations of the STE in CsI have not previously been identified. Based on transient absorption spectra of off-center STEs in many alkali halides, including the alkali iodides KI and RbI, the main electron transition of the off-center

STE occurs a few tenths of an eV lower energy than the F-center defect band in each crystal [4], [6], [7]. This is reasonable since the bound electron of the off-center STE can be approximately described as occupying a partially formed anion vacancy site. The electron transition absorption band of the STE typically has two or three times higher peak optical density than the hole transitions, partly because the electron band is narrower [4], [6], [7]. Likewise, based on studies of on-center STE transient absorption in NaI and NaBr [2], [8], the transitions of the loosely-bound Rydberg-like electron in the potential of the on-center hole can be expected to produce an intense and fairly narrow infrared absorption band farther in the infrared, e.g., around 0.16 eV (7.75 μm) in NaI [8]. The bound electron transitions provide a more distinct signature of whether an STE is on- or off-center than do the hole transition spectra. Furthermore the existence of the distinctive bound electron transitions are the spectral distinguisher of whether the ultraviolet hole transitions come from self-trapped holes or self-trapped excitons. Finding the infrared absorption bands of one or both STE configurations would supply an important piece to the STE model for CsI and set the stage for experimental probing of energy- and charge-carrier populations during a scintillator's excited phase. The transient absorption spectrum reported by Gafiatulina et al. was starting to rise as they approached their long-wavelength detector limit at 1130 nm [5]. They remarked that infrared absorption could be expected in the STE model and that the observed start of a rise could indicate it.

With regard to undoped CsI, the experiment which is the subject of our report has been able to use a laser-generated infrared continuum pulse to probe wavelengths out to 1600 nm in transient absorption. The use of a pump-probe laser technique also gives the present work a view of dynamics of absorbing states from 0.5 ps to 300 ps after bandgap excitation.

In thallium-activated CsI, transient absorption is interesting and useful for additional reasons. One of these can be broadly tied to the problem of nonproportionality between light yield and particle energy, and its role in limiting energy resolution. Current attempts to understand and model the dependence of light yield on excitation density along the ionizing particle track motivate a need to verify experimentally how much of the energy is transported as bound electron–hole pairs (excitons) and how much is transported as independent electrons and holes (either free or hopping among traps) which subsequently recombine [9], [10]. One needs to know whether the excitons exist free, self-trapped, or as excited activators (with mobility by resonant transfer or thermal transfer), and similarly for the independent charge carriers. Parts of the answers to these questions can be supplied by observing induced transient absorption under excitation conditions similar to those in the particle excitation of a scintillator.

In CsI:Tl, the first measurements of transient absorption induced by an electron pulse were reported in 2009 by Yakovlev et al. [11]. They used the same experimental set-up as for their work on undoped CsI [5]. The transient absorption data, principally acquired at 80 K, led them to conclude that the holes produced in CsI:Tl exist predominantly as self-trapped holes (possibly near Tl^+ or Tl^0 activators) and that the majority of excited electrons exist as the Tl^0 charge state of the activator on the nanosecond to microsecond time scale.

Because our pump-probe laser experiment can look farther into the infrared and shorter in time, we undertook measurements of CsI:Tl to add corroboration and some extension of the spectral and time ranges to the data of Yakovlev et al. [11]

II. EXPERIMENT

The excitation pulse is the second harmonic of an amplified Ti:Sapphire mode-locked laser operating at 820 nm. The excitation pulse has wavelength 410 nm, photon energy 3.02 eV, and a pulsewidth of ∼300 fs. To cross the 6-eV bandgap of CsI and produce electron–hole pairs throughout the interior of the sample, we depend on two-photon absorption of the 3.02-eV blue light. This method was chosen over one-photon excitation to avoid concentration of the deposited energy near the sample surface and to achieve sufficient total number of carriers spread nearly uniformly through the 3-mm sample thickness. It is estimated that free-carrier densities of roughly 10^{18} cm^{-3} were produced in these experiments. The excitation spot diameter was about 2 mm, chosen to be significantly larger than the 1-mm continuum probe spot. The pulse energy at 410 nm was about 400 μJ, corresponding to peak power density of 40 GW/cm^2.

For infrared measurements, the probe continuum was generated by focusing part of the 820-nm pulse in benzene, yielding a reasonably smooth light spectrum from visible out to 1600 nm in the infrared. After passing through the excitation spot on the sample and then through a monochromator, the probe pulse was detected by an InGaAs photodetector. The photodetector output for laser pulses at 10-Hz repetition rate was integrated by a Stanford Research Systems SR200 boxcar integrator. Thirty laser shots were averaged for each time step of the probe pulse delay line. The reference transmitted light level in absence of excitation (I_0) was taken as the average of measurements at 5- to 20-ps negative delay (probe pulse arriving before the excitation pulse). Since excitation and probe pulses repeated at 10 Hz, this method of measuring I_0 defines transient absorption in this experiment as that part of induced absorption which recovers within 0.1 s. That is, the absorption data and spectra reported here do not include induced permanent or long-term defect absorption.

For visible and ultraviolet absorption measurements in the range 730 to 300 nm, a water cell was used for continuum generation from the 820-nm fundamental, and a channel-plate-intensified optical multichannel analyzer was used to detect single-shot spectra of transmitted light. For doped CsI samples, 400 such spectra were averaged at each probe-pulse delay time. Similarly, for undoped samples, 100 laser shots were averaged. The visible spectra for all samples were the average of 10 shots. The reference spectrum, I_0, of transmitted light without sample excitation was recorded as an average with the 410-nm pump beam blocked. Unlike the infrared measurement of I_0, the method used for visible-uv measurements allows induced steady-state absorption to contribute. The spectrum of such absorption was measured with the probe continuum alone before and after a series of pump-pulse exposures equivalent to a run and was found to be negligible in these room-temperature measurements. In parts of the spectrum where luminescence was detectable in the
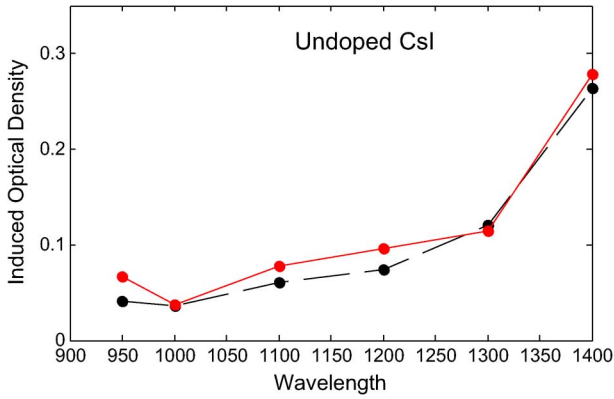
Fig. 1. Absorption induced by two-photon bandgap excitation of undoped CsI at room temperature, for probe delays of 3 ps (dashed curve) and 110 ps (solid curve) after excitation.
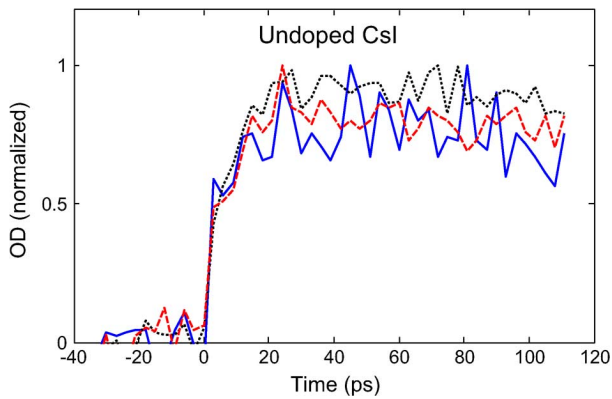

Fig. 2. Time dependences of the induced optical density in undoped CsI at wavelengths of 1000 nm (solid curve), 1400 nm (dashed line), and 1600 nm (dotted curve).
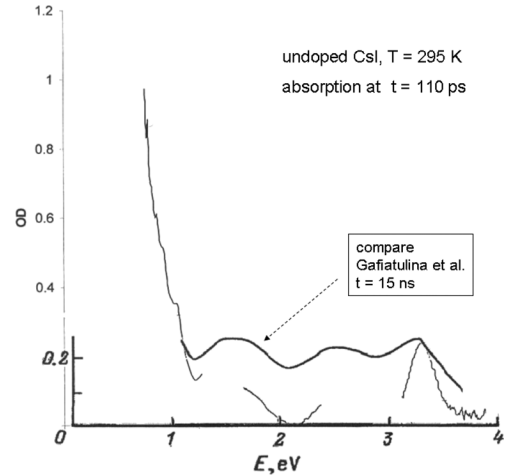

Fig. 3. Three segments showing infrared, visible, and ultraviolet transient absorption in undoped CsI at 110 ps after bandgap excitation at room temperature are plotted in the lighter line segments. The 15-ns transient absorption spectrum from [5] is overlaid in the heavier curve.
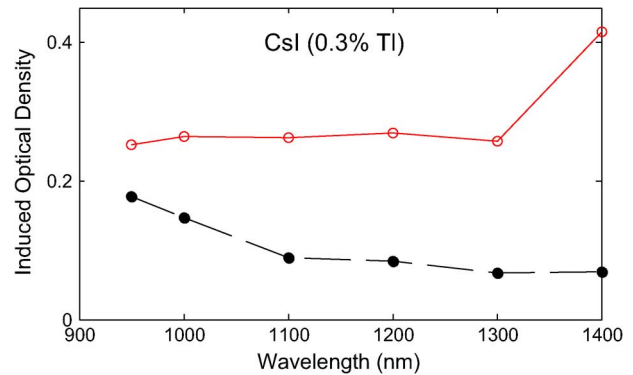

Fig. 4. Spectra of transient infrared absorption induced by two-photon bandgap excitation of 0.3 mole % Tl-doped CsI at room temperature, for probe delays of 3 ps (solid curve) and 94 ps (dashed curve) after excitation.

transmitted light, the luminescence spectrum was measured in a series of pump-only exposures and subtracted from the transmitted-light signal. In all measurements, it was necessary to use an optical filter to block the 820-nm pulse used in continuum generation from reaching the detector. This prevented acquiring data in the interval 900 to 730 nm. Likewise, a filter had to be used to block the 410-nm pump pulse from the detector, with the result that data in the interval 440 to 385 nm could not be acquired. All measurements for this report were made at room temperature

The CsI and CsI:Tl samples were grown at the Institute for Scintillation Materials in Kharkov, Ukraine, by the Stockbarger method in inert atmosphere. Concentrations of Tl were 0.3 mole % and 0.01 mole %. Doped and undoped samples were 4 mm and 3 mm thick, respectively, with polished surfaces.

III. RESULTS

Fig. 1 shows the spectra of transient infrared absorption induced by two-photon bandgap excitation of undoped CsI at room temperature, for probe delays of 3 and 110 ps after excitation. Time dependences of the induced optical density at 1000, 1400, and 1600 nm are shown in Fig. 2.

Fig. 3 shows the spectrum of infrared to ultraviolet transient absorption in undoped CsI at 110 ps after excitation at room temperature. As discussed above, the spectra have gaps surrounding the 820-nm laser fundamental and the 410-nm pump pulse. Overlaid on the data from this experiment is the spectrum measured at 15 ns after electron pulse excitation by Gafiatulina *et al.* [5].

Fig. 4 shows the spectra of transient infrared absorption induced by two-photon bandgap excitation of 0.3 mole % Tl-doped CsI at room temperature, for probe delays of 3 and 94 ps after excitation. Time dependence of the induced optical density at 950, 1000, 1300, and 1400 nm are shown in Fig. 5.

The transient infrared absorption spectrum and time dependences for CsI: 0.01% Tl are given in Figs. 6 and 7.

IV. DISCUSSION

In Fig. 3, the 110-picosecond induced absorption spectra of undoped CsI from the present measurement have been overlaid on the 15-ns spectra published by Gafiatulina *et al.* [5]. The onset of infrared absorption suggested by the turn-up at the long-wavelength limit of [5] does indeed continue rising strongly out to the 1600-nm limit of the present experiment. The qualitative appearance of the composite CsI spectrum is strikingly like the IR-UV spectrum of self-trapped excitons in NaI
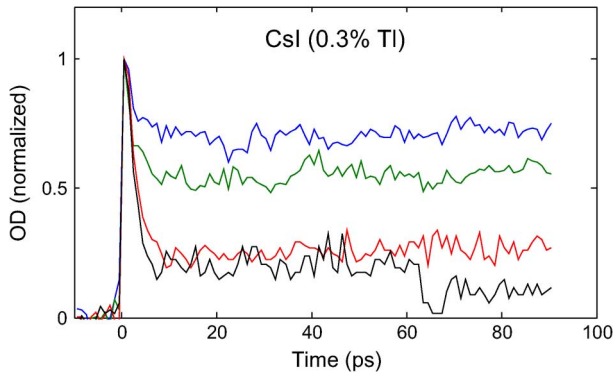
Fig. 5.   Time dependence of the induced optical density in CsI(0.3%Tl) at wavelengths (top to bottom) of 950, 1000, 1300, and 1400 nm.
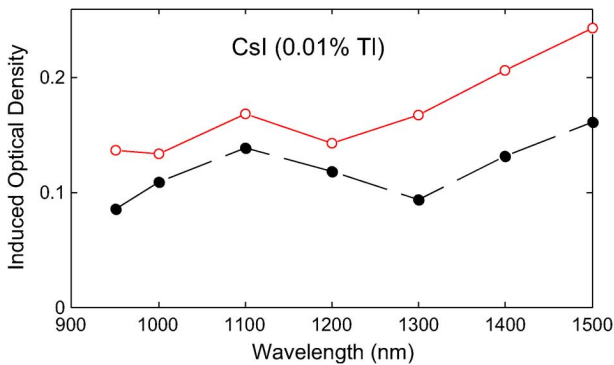

Fig. 6.   Absorption induced by two-photon bandgap excitation of CsI:(0.01% Tl) at room temperature, for probe delays of 3 ps (solid curve) and 110 ps (dashed curve) after excitation
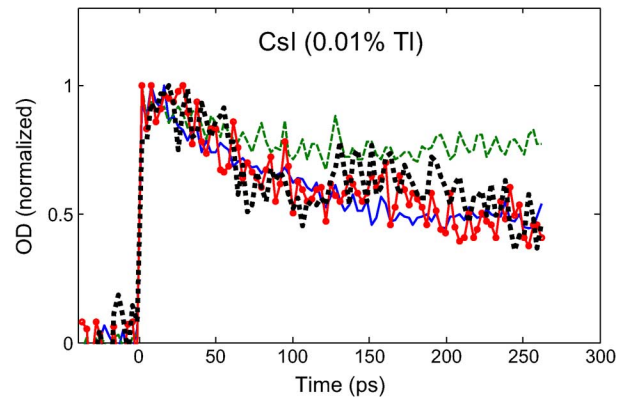

Fig. 7.   Time dependences of the induced optical density at 950 nm (solid curve), 1000 nm (dashed curve—showing least decay), 1300 nm (circles), and 1500 nm (dotted curve).

at 11 K measured by Edamatsu *et al.* [2]. The induced IR absorption in NaI was shown by Edamatsu *et al.* to be due to the on-center STE electron transition, i.e., excitation of the Rydberg-like outer electron around a V_k-like core. The peak of the IR absorption in NaI at 11 K is at 0.16 eV [8], and its rising edge at 0.35 eV was seen in [2] as dominating the smaller hole-excitation bands of the STE. In CsI, we have not yet found the peak of the infrared absorption, but the rising edge is near 0.8 eV rather than 0.35 eV. Part of this difference can be due to the fact that the present measurements are at room temperature and [2] reported measurements at 11 K. However, the difference is sufficiently large that we believe different STE configurations are being observed. Only the on-center STE has been seen in NaI, whereas Nishimura *et al.* found both on-center and off-center STEs in equilibrium in CsI at room temperature.

We suggest that the 0.8 eV rising edge in CsI is associated with the electron excitation band of the off-center STE. The F-center defect absorption band in CsI is at 1.4 eV. It is typical in other alkali halides that the strong transient absorption band associated with excitation of the bound electron in the partially-formed anion vacancy of the off-center STE occurs a few tenths of an eV lower energy than the F band.[6]. In RbI, for example, the electron transitions of the STE are at 1.2 and 1.4 eV, compared to the F band at 1.75 eV. If the transient absorption band at or below 0.8 eV in CsI is correctly assigned as the electron band of the off-center STE, then the 1.7-eV transient absorption band should be assigned to the $\sigma_u \rightarrow \pi_g$ hole transi-

tion of the STE. Furthermore, since the on-center STE has already been identified in CsI from the luminescence data [1], the identification made above should lead us to expect yet another strong absorption band farther in the infrared corresponding to the on-center STE in NaI, i.e., with peak around 0.16 eV. In future work, we intend to use an optical paramatric amplifier for deeper infrared probe pulses to reveal the full spectrum of the infrared absorption band rising at 0.8 eV and to search for another one at lower energy.

The infrared absorption might be simply free-carrier absorption. However, since CsI is known already to exhibit self-trapped excitons, the STE remains the leading candidate to explain infrared transient absorption. Lifetime, spectrum, and temperature dependence data from future work can give positive identification.

The 2.5-eV transient absorption was assigned by Gafiatulina *et al.* [5] to $\sigma_u \rightarrow \sigma_g$ hole transitions of the H- or V_k-like halogen core of off-center and on-center STEs respectively. They regarded the 3.4 eV UV transient absorption peak of pure CsI as being at an energy different from usual H- and V_k-like hole transitions of the STE, and so suggested that it may be associated with a tri-iodide configuration of the STE. The 3.4-eV and 2.5-eV transient absorption bands decay at the same rate from 15 to 500 ns at 80 K. If the bands are due to different STE lattice configurations, it requires either coincidence or thermal equilibrium at 80 K to have the same shared decay time. Incidentally, the STE spectrum of RbI exhibits a similar pair of ultraviolet hole-transition bands at 3 eV and 3.5 eV. In RbI also, all these transitions share the same decay time at 9 K, in which case thermal equilibrium of two configurations is very unlikely to account for the two bands with identical lifetime.

Instead, we want to look again at how the STE absorption band energies line up with V_k transition energies. This was plotted for 9 alkali halides including 3 fcc alkali iodides in Fig. 8 of [6]. In the majority of cases, the STE ultraviolet band is found at slightly *higher* energy than the corresponding V_k band, in fact moving close to the H band in the same crystal. The ultraviolet V_k band in KI and RbI [6] and CsI [11], [12] is at 3 eV. Anticipating the typical case of finding the ultraviolet STE band about 0.3 eV higher than the V_k band [6], we should regard the 3.4-eV absorption band in CsI as the expected $\sigma_u \rightarrow \sigma_g$ hole band of

the STE. It does not require appealing to a new tri-iodide configuration, although the halogen crowdion core of an off-center STE does have a tri-halide sharing of the hole. It seems to us to be the lower-energy 2.5-eV hole band in CsI that is harder to assign.

If the hole transitions of the STE in CsI were to be modeled on the I_2^- molecule ion with inversion symmetry and axial rotation symmetry $(D_{\infty h})$, there would be only two allowed transitions within the manifold derived from iodine p-states: the $\sigma_u \rightarrow \sigma_g$ transition (argued above to be at 3.4 eV) and the $\sigma_u \rightarrow \pi_g$ transition (observed 1.7-eV band in good agreement with the $\sigma_u \rightarrow \pi_g$ V_k band). The observed 2.5-eV transient absorption band in CsI lies between these two, as does the energy of the third "possible" transition from a σ_u hole within the p-derived molecular orbitals in $D_{\infty h}$: $\sigma_u \rightarrow \pi_u$. But this dipole transition is parity-forbidden in the presence of inversion symmetry as possessed by the V_k center or on-center STE. In a moderately off-center STE such as occurs in CsI, the inversion symmetry and hence the parity-forbiddenness is lost, but one may still expect molecular orbitals corresponding approximately in energy to what had been π_g, π_u, and σ_g excited orbitals of the V_k center. This is speculative until verified by electronic structure calculations for the off-center STE in CsI, but it points to a possible origin for three hole transitions within moderately off-center STEs.

The relevance of these proposed identifications of transient absorption in pure CsI for our interest in activated CsI:Tl scintillators is that 0.8-eV induced absorption is likely to be a distinctive signature of self-trapped excitons (particularly in future work when spectrum extension allows identification of the entire band). Any one of the three visible-uv transient absorption bands is a signature of the sum of self-trapped hole and self-trapped exciton populations. Careful measurement of the spectral shapes and peak positions of the UV bands might be able to distinguish between STE and STH populations, but the consideration of infrared and ultraviolet absorption together can best sort out the STE and STH contributions.

In Fig. 4, the transient infrared absorption spectra of CsI:(0.3% Tl) are plotted at 3 and 94 ps after excitation. The 94-ps spectrum contrasts sharply with what we saw in undoped CsI. In CsI:0.3%Tl, the induced absorption decreases from 950 nm toward 1400 nm. Whether the induced infrared absorption in undoped CsI is ascribed to STEs or to free carriers, Fig. 4 would indicate that neither of them are present in significant number at 94 ps (or even 5 ps) after bandgap excitation of CsI:0.3% Tl. Instead, the one feature attributable to electrons resulting from bandgap excitation is the Tl^0 peak at 1.35 eV, as seen clearly by Yakovlev *et al.* [11]. We interpret the rising absorption from 1400 nm toward 950 nm as consistent with the long wavelength edge of the Tl^0 band having its peak at 920 nm. Thus, our infrared measurements at delays longer than 5 ps are in agreement with the conclusion by Yakovlev *et al.* that bandgap excitation of CsI:Tl produces mainly self-trapped holes, and electrons trapped on Tl^+ to produce Tl^0 [11].

However, the first 5 ps is a different story. As shown in Figs. 4 and 5, the infrared spectrum in CsI:(0.3% Tl) can be considered consistent with STE population similar to undoped CsI for the first ~5 ps, thereafter transforming to the V_k and Tl^0

populations discussed above and in [11]. This raises interesting questions for theoretical study of how much energy transport might occur by self-trapped exciton diffusion in the first 5 ps at room temperature, and of how initially-formed STEs can ionize so quickly at room temperature to yield holes and electrons that are self-trapped and captured by Tl^+, respectively. The shallow binding energy of the on-center STE and room-temperature equilibration of on- and off-center STEs in CsI may be important for the latter question.

Fig. 6 for lightly-doped CsI:(0.01% Tl) shows the long-wavelength part of the infrared absorption decaying more than the shorter-wavelength part. This is qualitatively a weaker version of the trend seen in Fig. 4 for CsI:(0.3% Tl). Fig. 7 shows that the absorption partly decays on a time scale of about 100 ps in CsI:(0.01% Tl), compared to 5 ps in the more heavily doped sample (Fig. 5). According to the interpretation we have given to the infrared absorption, the behavior in Figs. 4–7 suggests that the rate of conversion and ultimate degree of conversion of initially produced self-trapped excitons to independent trapped carriers scales with increasing thallium concentration.

It is interesting that NaI:Tl, CsI:Tl, and CsI:Na are the only three scintillator materials found by Valentine *et al.* [13] and more recently confirmed along with $SrI_2:Eu^{2+}$ in [14] to exhibit strong nonlinearity of light yield versus electron energy at both low and high dE/dx, i.e., characteristically sloping significantly upward from low dE/dx, reaching a peak, and then falling at high dE/dx characteristic of track ends. All other measured scintillators either exhibit only the roll-off at high dE/dx, or exhibit it in combination with a much weaker rising slope at low dE/dx. A phenomenological model [9], [10] based on 1st- and second-order radiative decay in the presence of first- through third-order nonradiative decay shows that the "hump" in nonlinearity of light yield will always result unless the coefficient of second-order radiative decay, a_2, is negligible compared to the monomolecular radiative coefficient a_1, or unless $a_1/a_2 = 1/a_3$, where a_3 is the coefficient of third-order nonradiative decay.

Thus it is significant for understanding and modeling nonproportional scintillator response to have an experimental measure of the relative roles of independent charge carriers recombining by second-order kinetics and of excitons or other first-order transport mechanisms in producing luminescence. This report has provided an illustration of the utility of transient optical absorption in achieving such data, and along with [11] concludes that in CsI:(0.3% Tl) after the first 5 ps, the excitation energy is contained mainly in the form of independent electrons trapped as Tl^0 and of holes self-trapped.

Electron pulse induced transient absorption and luminescence in NaI:Tl and KI:Tl were studied by Dietrich *et al.* [15]. They concluded that "... nearly all [~ 95%] of the energy transport in KI(Tl) occurs by [independent] electron–hole diffusion...." It was more difficult to do complete transient absorption studies on NaI:Tl because the luminescence tended to overwhelm the probe flash lamp, but from available absorption data and luminescence decay kinetics, they reached a similar conclusion regarding NaI:Tl [15]. The NaI:Tl luminescence decay at room temperature under electron pulse excitation to a density of 10^{18} e–h pairs/cm^3 was plotted on a log-log scale and

can be seen to obey second-order kinetics over five decades of intensity after exponential decay in the first decade [15]. This is consistent with binary electron and hole diffusion in the form of Tl^0 and Tl^{++} trapped charges accounting for the major recombination luminescence route. The present study and [11] have suggested a similar conclusion in regard to CsI:Tl.

ACKNOWLEDGMENT

REFERENCES

[1] H. Nishimura, M. Sakata, T. Tsujimoto, and M. Nakayama, "Origin of the 4.1-eV luminescence in pure CsI scintillators," *Phys. Rev. B*, vol. 52, pp. 2167–2172, Jan. 1995.

[2] K. Edamatsu, M. Sumita, S. Hirota, and M. Hirai, "Transient absorption due to self-trapped excitons in NaBr and NaI," *Phys. Rev. B*, vol. 47, pp. 6747–6750, Mar. 1993.

[3] K. Kan'no, K. Tanaka, and T. Hayashi, "New aspects of intrinsic luminescence in alkali halides," *Rev. Solid State Sci.*, vol. 4, p. 383, 1990.

[4] K. S. Song and R. T. Williams, *Self-Trapped Excitons*. Berlin, Germany: Springer-Verlag, 1993, ch. 5.

[5] E. S. Gafiatulina, S. A. Chernov, and V. Y. Yakovlev, "Creation of excitons and defects in a CsI crystal during pulsed electron irradiation," *Phys. Solid State*, vol. 40, pp. 586–590, Apr. 1998.

[6] R. T. Williams and M. N. Kabler, "Excited-state absorption spectroscopy of self-trapped excitons in alkali halides," *Phys. Rev. B*, vol. 9, pp. 1897–1907, Feb. 1974.

[7] R. G. Fuller, R. T. Williams, and M. N. Kabler, "Transient optical absorption by self-trapped excitons in alkali halide crystals," *Phys. Rev. Lett.*, vol. 25, pp. 446–449, Aug. 1970.

[8] K. Edamatsu and M. Hirai, "Infrared studies of self-trapped excitons," *Mater. Sci. Forum*, vol. 239–241, pp. 525–530, 1997.

[9] G. Bizarri, W. W. Moses, J. Singh, A. N. Vasil'ev, and R. T. Williams, "An analytical model of nonproportional scintillator light yield in terms of recombinations rates," *J. Appl. Phys.*, vol. 105, pp. 044507-1–044507-15, Feb. 2009.

[10] G. Bizarri, W. W. Moses, J. Singh, A. N. Vasil'ev, and R. T. Williams, "Simple model relating recombination rates and non-proportional light yield in scintillators," *Phys. Stat. Sol. (c)*, vol. 6, pp. 97–100, Oct. 2008.

[11] V. Yakovlev, L. Trefilova, and A. Meleshko, "Time-resolved optical spectroscopy of CsI(Tl) crystals by pulsed electron beam irradiation," *J. Lum.*, vol. 129, pp. 790–796, Feb. 2009.

[12] J. M. Spaeth, W. Meise, and K. S. Song, "The nature of X-ray induced luminescence and the hole centers of CsI:Tl studied by optically detected electron paramagnetic resonance," *J. Phys. C*, vol. 6, p. 3999, Feb. 1994.

[13] W. Mengesha, T. Taulbee, B. Rooney, and J. Valentine, "Light yield nonproportionality of CsI(Tl), CsI(Na), and YAP," *IEEE Trans. Nucl. Sci.*, vol. 45, p. 456, Nov. 1997.

[14] L. Ahle, G. Bizarri, L. A. Boatner, N. J. Cherepy, W.-S. Choong, W. W. Moses, S. A. Payne, K. Shah, S. Sheets, and B. W. Sturm, "Studies of non-proportionality in alkali halide and strontium iodide scintillators using SLYNCI," in *Proc. Mater. Res. Soc. Spring 2009 Meet.*, San Francisco, Apr. 2009, (LLNL-PROC-412818), accepted for publication.

[15] H. B. Dietrich, A. E. Purdy, R. B. Murray, and R. T. Williams, "Kinetics of self-trapped holes in alkali-halide crystals: Experiments in NaI(Tl) and KI(Tl)," *Phys. Rev. B*, vol. 8, pp. 5894–5901, Dec. 1973.