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Highlights for “Characterization of light output and scintillation emission in CsI(Tl), NaI(Tl), and LaBr<sub>3</sub>(Ce) under isostatic pressure”

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- Isostatically pressurized CsI(Tl), NaI(Tl), and LaBr<sub>3</sub>(Ce) using custom instrument
- Observed changes in light output, decay time, and emission spectra from 0 to 800 MPa
- Experimental data compared to results derived from an analytical model
- Scintillation properties are pressure (and hence, structurally) dependent



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# Characterization of light output and scintillation emission in CsI(Tl), NaI(Tl), and LaBr<sub>3</sub>(Ce) under isostatic pressure

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## ABSTRACT

The application of high isostatic pressure has been known to affect the electronic band structure of the host lattice and the electronic states of luminescence centers in scintillators. Using pulse-height gamma-ray and photoluminescence spectroscopy, the scintillation light output, decay time, and emission behavior of CsI(Tl), NaI(Tl) and LaBr<sub>3</sub>(Ce) were studied under high isostatic pressure up to 800 MPa. The light output behavior of CsI(Tl) was found to exhibit a different trend than those observed by NaI(Tl) and LaBr<sub>3</sub>(Ce), explained by shifts in the photoluminescence wavelengths with increased applied pressure. Scintillation decay times were also observed to shorten with pressure. The observed trends in light output and decay times are explained and compared to estimations by analytical models.

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1 **1. Introduction**

2 Inorganic scintillators are compounds that luminesce when excited  
3 by ionizing radiation. These materials are increasingly used as  
4 radiation detectors in a number of fields, including nuclear medicine,  
5 high energy physics, and homeland security. The ongoing quest for  
6 novel scintillators with improved properties such as light yield, decay  
7 time, energy resolution, and light yield proportionality has stimulated  
8 efforts to more clearly elucidate the relationship between scintillator  
9 performance and a material's structure and chemical composition [1].

10 The application of high isostatic pressure has been shown to affect  
11 a host crystal's electronic band structure as well as the electronic states  
12 of the luminescence centers [2, 3]. Furthermore, band structure  
13 modeling by Setyawan et al. [4] predicts a relationship between light  
14 yield proportionality and applied isostatic pressure. Pressure also  
15 affects the migration and recombination properties of free charge  
16 carriers and excitons [3, 5-8] and hence, light output. The few  
17 published pressure studies to date, however, have been insufficient for  
18 establishing a comprehensive relationship between scintillation  
19 performance and structure. It is clear that more experimental work is  
20 needed to elucidate such a relationship.

21 In this study, the photoluminescence spectra, light output, and  
22 energy resolution of three scintillators, CsI(Tl), LaBr<sub>3</sub>(Ce), and

23 NaI(Tl), were characterized up to isostatic pressures between 600-800  
24 MPa using a custom-designed high-pressure instrument. The decay  
25 times of CsI(Tl) and LaBr<sub>3</sub>(Ce) were also investigated.

26 **2. Experimental setup and methods**

27 CsI(Tl), LaBr<sub>3</sub>(Ce), and NaI(Tl) were characterized in this study  
28 (Table 1). Each 1 cm<sup>3</sup>-sized sample had five ground faces and one  
29 polished face. The samples were wrapped with a specular reflector,  
30 Vikuiti Enhanced Specular Reflective Film (ESR, trademark of 3M),  
31 to optimize the light collection. This was important since the presence  
32 of an optical window prevented direct coupling between the sample  
33 and the photodetector.

34 The pressure instrument consists of an air-driven, two-stage  
35 compressor utilizing heptane as the compression fluid. The pressure

Table 1.  
Structural and luminescence properties for the crystals used in this study.

Crystal	Bulk modulus [GPa]	Emission wavelength [nm]	Light output [ph/MeV]	Decay time [μs]
CsI(Tl)	12.6 [9]	540 [10]	65k [10]	0.8/6 [10]
LaBr <sub>3</sub> (Ce)	N/A	360/380 [11]	60k [11]	0.023 [11]
NaI(Tl)	15.1 [9]	415 [10]	38k [10]	0.23/1 [10]

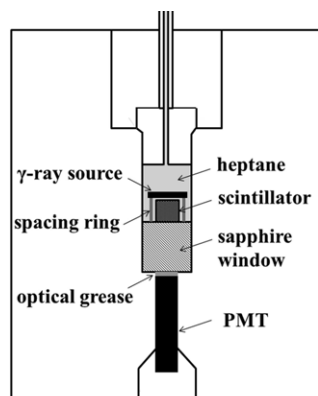


Fig. 1. Scheme of the pressure vessel and associated components. A photomultiplier (PMT) (shown) or optical probe can be coupled to the sapphire window.

1 vessel accommodates samples up to 5 cm<sup>3</sup> in size and is equipped with  
 2 a sapphire optical window. The excitation source, <sup>137</sup>Cs, is placed on  
 3 top of the sample, which sits on the sapphire window (Fig. 1). Details  
 4 about the pressure system and its performance characteristics can be  
 5 found in Gaumé et al. [12].

6 The scintillation light was collected by a Hamamatsu R4141  
 7 photomultiplier tube (PMT) coupled to the exterior of the sapphire  
 8 window with silicone optical grease (Bicron BC-630). A PMT voltage of  
 9 -1 kV was selected as the bias voltage. The output signals were  
 10 amplified with a Canberra 2022 amplifier using shaping times of 4, 0.5  
 11 and 1 μs for CsI(Tl), LaBr<sub>3</sub>(Ce), and NaI(Tl), respectively. The  
 12 selected shaping times were sufficiently long compared to the  
 13 scintillation decay times in the pressure ranges studied. The resultant  
 14 signals were processed with an Amptek MCA-8000 multichannel  
 15 analyzer. A satisfactory signal-to-noise ratio was ensured by collecting  
 16 at least 5,000 to 10,000 counts per photopeak. These were fit using a  
 17 Gaussian function and an exponential background to determine the  
 18 centroid and full-width at half-maximum.

19 For the light output measurements, the system was first pressurized  
 20 up to the maximum pressure, and then held and lowered to a selected  
 21 pressure using a pressure release valve. The relative light output was  
 22 determined by comparing the centroid at a given pressure to its value  
 23 at 0 MPa.

24 The scintillation decay time under <sup>137</sup>Cs excitation was  
 25 characterized at each pressure by recording 1,600 decay traces directly  
 26 from the PMT output using a Yokogawa DL6154 digital oscilloscope  
 27 and a 50 Ω terminator to match the cable impedance. A pulse pile-up  
 28 rejection algorithm was implemented using a ROOT macro  
 29 (<http://root.cern.ch>). The decay traces were fit with double and single  
 30 exponential functions for CsI(Tl) and LaBr<sub>3</sub>(Ce), respectively. The  
 31 scintillation decay time for a given pressure was determined by  
 32 averaging the calculated values derived from the fitted traces.

33 Since the pressure instrument is not compatible with conventional  
 34 x-ray luminescence measurements and the activity of the <sup>137</sup>Cs  
 35 excitation source was low, photoluminescence spectra were collected  
 36 instead of scintillation emission spectra. This was accomplished by  
 37 exciting each sample with monochromatic light, λ<sub>exc</sub> = 300 nm, from  
 38 a 35W Xenon lamp using an Ocean Optics QE 65000 spectrometer  
 39 with a 10 second integration time. Both the excitation and the emission  
 40 were delivered and collected, respectively, using a  
 41 reflection/backscattering optical probe (Ocean Optics, R600-7-  
 42 UV/125F). The excitation wavelength of 300 nm was chosen after  
 43 examining the excitation spectra of CsI(Tl) [13-14], NaI(Tl) [15], and  
 44 LaBr<sub>3</sub>(Ce) [16-17]. At 300 nm, overlap between the excitation and  
 45 photoluminescence spectra was avoided.

46 Due to the hygroscopic nature of NaI(Tl) and LaBr<sub>3</sub>(Ce), these  
 47 samples were stored in anhydrous heptane until transfer into the  
 48 sample chamber of the pressure vessel.

### 49 3. Results

50 The scintillation light output of CsI(Tl), LaBr<sub>3</sub>(Ce), and NaI(Tl)  
 51 under applied pressure are shown in Fig. 2. At 800 MPa, the light  
 52 output of CsI(Tl) increased by 40% while the light output of LaBr<sub>3</sub>(Ce)  
 53 and NaI(Tl) decreased by approximately 15% and 40%, respectively.

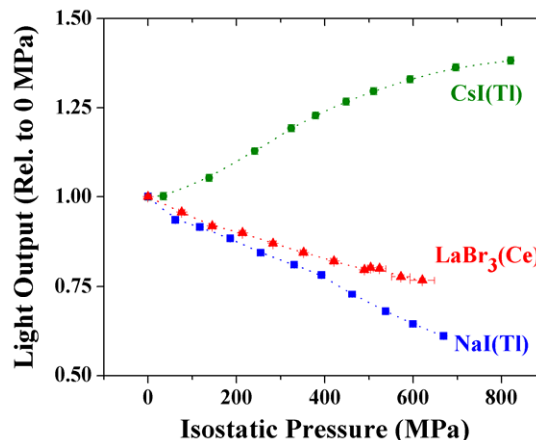


Fig. 2. Light output as a function of isostatic pressure for three different scintillators.

54 The scintillation decay times for CsI(Tl) and LaBr<sub>3</sub>(Ce) were  
 55 determined at regular pressure intervals from 0 to 840 MPa and from 0  
 56 to 497 MPa, respectively. Table 2 shows the measured scintillation  
 57 decay times and intensities for CsI(Tl) and LaBr<sub>3</sub>(Ce). The value in the  
 58 last column of CsI(Tl) corresponds to a fit with one single exponential.  
 59 From Fig. 3, which shows the change in decay time relative to the  
 60 values at ambient pressure, the decay time of CsI(Tl) was observed to  
 61 decrease by 30% of its ambient pressure value. The decay time of  
 62 LaBr<sub>3</sub>(Ce) decreased by less than 10% when pressurized up to 350  
 63 MPa, and remained fairly constant around 23 ns as the applied  
 64 pressure was raised to 500 MPa.

65 The photoluminescence response of CsI(Tl), NaI(Tl), and  
 66 LaBr<sub>3</sub>(Ce) under 300 nm excitation of the Tl<sup>+</sup> and Ce<sup>3+</sup> activator ions  
 67 are shown as a function of pressure in Figs. 4, 5, and 6. At ambient  
 68 pressure, the photoluminescence for CsI(Tl), NaI(Tl), and LaBr<sub>3</sub>(Ce)  
 69 peak around 550 nm (Fig. 4), 340 and 430 nm (Fig. 5), and 355 and  
 70 390 nm (Fig. 6), which is in agreement with the values  
 71 reported in literature [14, 18, 19-21]. The photomultiplier (PMT)'s  
 72 quantum efficiency is also shown on these plots for comparison. The  
 73 arrows indicate the direction of shift in photoluminescence  
 74 wavelengths and change in intensity with applied pressure.

75 Less than 5% degradation in light output was observed after the  
 76 application of isostatic pressure and the scintillation decay times and  
 77 photoluminescence behavior at 0 MPa were also found to be  
 78 reproducible before and after pressurization. Furthermore, no visible  
 79 damage such as cracking or plastic deformation (i.e. dimensional  
 80 changes) was observed in the crystals after applied pressure.

### 81 4. Discussion

82 Initial examination of the variation of light output with pressure for  
 83 CsI(Tl), NaI(Tl) and LaBr<sub>3</sub>(Ce) reveals that CsI(Tl) exhibits a different  
 84 behavior than NaI(Tl), and LaBr<sub>3</sub>(Ce). Since the amount of light  
 85 collected depends on the quantum efficiency of the photomultiplier  
 86 tube, the photoluminescence response for each material was collected  
 87 to verify whether the observed changes in light output were due to  
 88 changes in light output intensity or changes in the overlap between the  
 89 photoluminescence wavelengths and the PMT quantum efficiency.

Table 2.

Measured scintillation decay time constants and intensities for CsI(Tl) and LaBr<sub>3</sub>(Ce) under isostatic pressure. Typical uncertainties are shown on the bottom row.

Pressure (MPa)	CsI(Tl)					LaBr <sub>3</sub> (Ce)	
	I <sub>1</sub>	τ <sub>1</sub> (μs)	I <sub>2</sub>	τ <sub>2</sub> (μs)	Single τ (μs)	Pressure (MPa)	τ (ns)
0	0.76	0.87	0.24	2.5	1.28	0	25.1
140	0.74	0.79	0.26	2.4	1.24	77	24.1
245	0.71	0.67	0.29	2.1	1.17	145	23.7
385	0.54	0.50	0.46	1.6	1.16	217	23.4
455	0.68	0.53	0.32	1.8	1.08	283	23.5
518	0.71	0.51	0.29	1.8	1.03	357	22.8
602	0.71	0.43	0.29	1.6	0.98	427	22.9
700	0.69	0.40	0.28	1.5	0.95	497	22.9
840	0.67	0.41	0.23	1.6	0.9	-	-
± 1	± 0.01	± 0.02	± 0.01	± 0.02	± 0.02	± 1	± 0.02

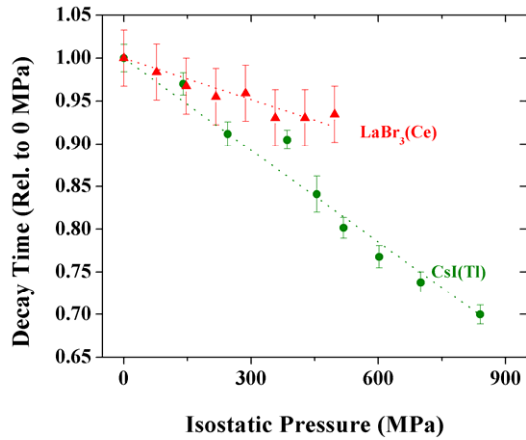


Fig. 3. Scintillation decay time as a function of isostatic pressure for CsI(Tl) and LaBr<sub>3</sub>(Ce).

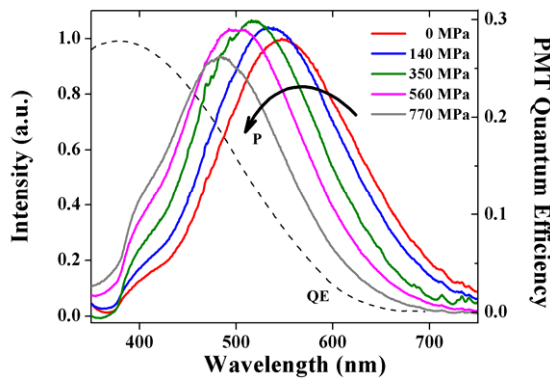


Fig. 4. Photoluminescence response as a function of isostatic pressure for CsI(Tl).

1 From Fig. 4, the blue-shift of the CsI(Tl) photoluminescence  
2 towards regions of higher PMT quantum efficiency has a greater  
3 influence on the light output than the decrease in intensity with  
4 pressure. Consequently, the light output was observed to increase (Fig.  
5 2). For NaI(Tl), the decrease in the 430 nm photoluminescence  
6 intensity offsets the contributions to the light output from the small  
7 blue-shift and the slight increase in the 340 nm intensity. In the case of

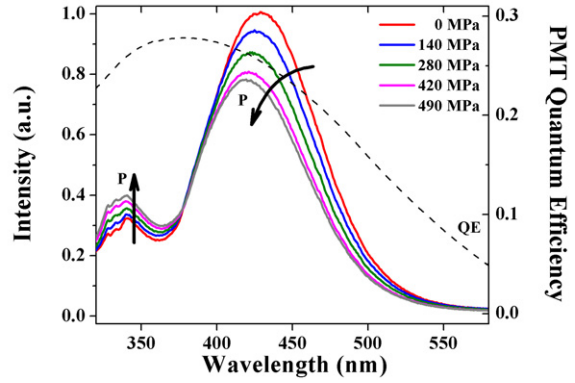


Fig. 5. Photoluminescence response as a function of isostatic pressure for NaI(Tl).

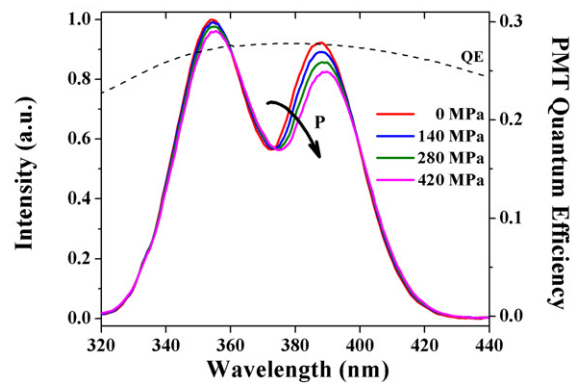


Fig. 6. Photoluminescence response as a function of isostatic pressure for LaBr<sub>3</sub>(Ce).

8 LaBr<sub>3</sub>(Ce), the photoluminescence peaks are centered with respect to  
9 the PMT quantum efficiency. The intensity of the 350 nm peak  
10 remains constant while the intensity of the 380 nm peak decreases,  
11 resulting in a decrease in light output (Fig. 6).

12 For a more quantitative analysis, the scintillation light output can  
13 be compared with the estimated light output, LO<sub>est</sub>, of these  
14 scintillators with pressure using the following formula:

$$15 \quad LO_{est}(P) = \int QE(\lambda) EM(\lambda, P) d\lambda \quad (1)$$

16 where  $QE(\lambda)$  is the PMT quantum efficiency and  $EM(\lambda, P)$  is the  
17 measured emission spectra resulting from gamma-ray excitation. The  
18 result of this convolution can be used to estimate the expected  
19 scintillation light output behavior. The pressure-dependent  
20 photoluminescence spectra (Figs. 4 to 6) were used for  $EM(\lambda, P)$  in  
21 Eqn. (1) since literature shows no significant differences between the  
22 spectra resulting from gamma-ray excitation and those from UV-  
23 excited photoluminescence for CsI(Tl) [13, 20-23], NaI(Tl) [15, 20,  
24 24], and LaBr<sub>3</sub>(Ce) [11, 17, 25] at ambient pressure. Indeed,  
25 comparison of the measured photoluminescence spectra with those in  
26 literature [11, 13, 15, 17, 20-25] for the three materials at 0 MPa (Figs.  
27 4 to 6) confirm that the transitions relevant to the scintillation process  
28 (Tl<sup>+</sup> and Ce<sup>3+</sup> to their respective ground states) were accessed with the  
29 300 nm excitation. Note that while changes in light transmission were  
30 not considered, the estimated light output, LO<sub>est</sub>, in Fig. 7 exhibited  
31 behavior similar to the scintillation light output (Fig. 2). Values fall  
32 within a 15% margin of agreement.

33 The estimated decay times can also be predicted from the peak  
34 centroid of emission  $\lambda_m$ . Yanagida et al. [26] and Dorenbos [16]  
35 showed that in photoluminescence, the decay time can be analytically  
36 deduced as:



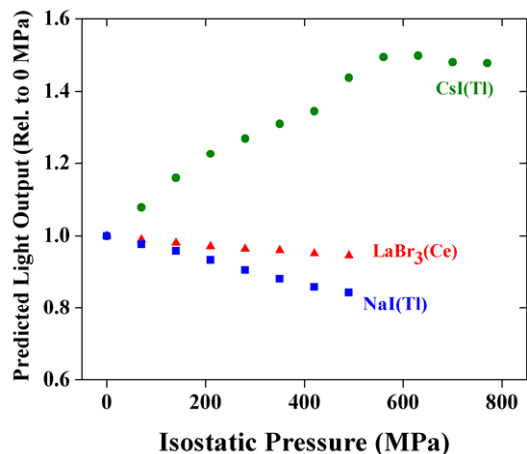


Fig. 7. Estimated light output using Eq. 1 for CsI(Tl), LaBr<sub>3</sub>(Ce), and NaI(Tl).

$$\Gamma = 1/\tau \sim (1/9)(n/\lambda^3)(n^2+2)^2 \sum |<f|\mu|i>|^2 \quad (2)$$

where  $\Gamma$ ,  $\tau$ ,  $n$ , and  $\lambda$  represent the decay rate of an excited state, decay time, refractive index, and photoluminescence wavelengths, respectively.  $|i\rangle$  and  $|f\rangle$  are the initial and final states of the transition and  $\mu$  is the dipole operator. This equation predicts a shorter decay time with a blue shift of emission wavelength and increase of the refractive index. It should be stated that the phenomena of photoluminescence is fundamentally different from that of scintillation. Photoluminescence decay time primarily describes the relaxation time of the emission center, whereas scintillation decay time describes this process in addition to other interactions with the host lattice during the scintillation mechanism such as charge carrier migration. However, a recent study by Yanagida et al. on oxides and fluorides doped with Ce<sup>3+</sup>, Pr<sup>3+</sup>, and Nd<sup>3+</sup> reveals that the differences between the scintillation and photoluminescence decay times are small, and that even in scintillation decay where energy migration occurs from the host lattice to the emission center, the emission process from the excited state of the ground state is dominant [26]. Thus, given this finding, the Eqn. (2) can be used to determine the photoluminescence decay time as an estimation of the scintillation decay time for LaBr<sub>3</sub>(Ce). This equation has also been used to describe the scintillation decay time of LaBr<sub>3</sub>(Ce) elsewhere in [16]. It is less obvious whether Eqn. (2) is also suitable for approximating the scintillation decay time of NaI(Tl) and CsI(Tl) since no comparison studies similar to those of [26] have been performed on these two materials. However, since the scintillation and photoluminescence decay times are 250 and 220 ns for NaI(Tl), respectively, and 700 and 560 ns for CsI(Tl), respectively [20], Eqn. (2) was applied to determine whether the photoluminescence decay would also be a good estimate of the scintillation decay.

Since no measurements were available for the pressure-dependent refractive index of LaBr<sub>3</sub>(Ce), the predicted values for this material do not take into account the change in the index of refraction with pressure. The pressure-dependent refractive indices for NaI(Tl) and CsI(Tl) were substituted with those for NaI and CsI measured by Johannsen et al. [27]. Finally, the last term, which is the strength of the transition or the probability of transition, was assumed to be constant for all three materials. Tsujimoto et al. [3] estimated that for CsI(Tl), the last term is not strongly dependent on pressure because the lattice constant is reduced by only 2% at 1 GPa. By applying the same logic for NaI(Tl) and LaBr<sub>3</sub>(Ce), in which even smaller changes in the lattice parameter are expected, the last term was also assumed constant in the analysis for these two materials.

The estimated photoluminescence decay times normalized to ambient pressure are shown in Fig. 8. Despite the

photoluminescence and scintillation decays being comparable at ambient pressure for LaBr<sub>3</sub>(Ce), the two responses deviate with applied isostatic pressure. This is possibly due to unaccounted changes in the refractive index with pressure. On the other hand, for CsI(Tl), the estimated photoluminescence decay response provides a good approximation of the scintillation decay time. We can learn a few interesting things from this latter result for CsI(Tl). Recall from the earlier discussion that photoluminescence and scintillation phenomena are fundamentally different since photoluminescence involves lifetime and relaxation of the emission center, whereas the scintillation decay time includes this process as well as the other interactions with the host lattice and transfer of charge carriers to the emission center during the scintillation mechanism [26]. This is the cause of the difference in measured photoluminescence and scintillation decay times at ambient pressure, as previously mentioned. However, by examining the normalized photoluminescence and scintillation decay responses for CsI(Tl) with applied pressure (Fig. 8), it can be deduced from the similar trends that the evolution of the excited and ground state levels evolve in the same manner with applied pressure, and that other host-charge related interactions occurring in the scintillation interaction are less significant compared to the relaxation behavior of the Tl<sup>+</sup> emission center.

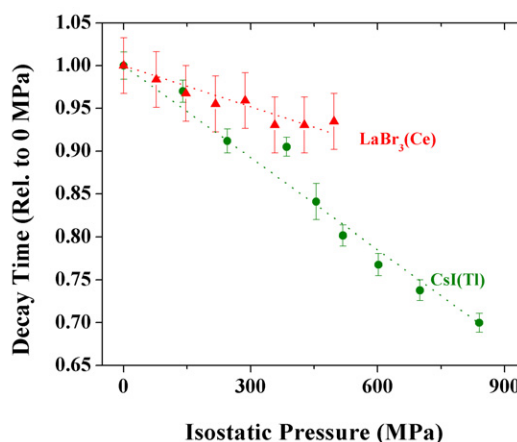


Fig. 8. Normalized photoluminescence decay time as a function of isostatic pressure for CsI(Tl) and LaBr<sub>3</sub>(Ce).

Finally, the overall decrease in both the scintillation and photoluminescence decay times of CsI(Tl) and LaBr<sub>3</sub>(Ce) (Fig. 3) suggest increasing the application of isostatic pressure in our investigated range facilitates the recombination and relaxation process at the emission center. Understanding the precise manner in which this occurs requires further investigation.

In the meantime, however, the scintillation light output and scintillation decay time trends in this study can be related to what is previously known about the emission center and its behavior with applied pressure. While few studies are published regarding the influence of pressure on the emission of LaBr<sub>3</sub>(Ce), the halides have been previously investigated. Firstly, it is well understood that the application of pressure strongly affects the overlap of adjacent orbitals [28]. For example, for the thallium-doped halides, when pressure is applied, the repulsive energy between the thallium and halide ions is increased due to greater orbital overlap between the ions. This modifies the energy states of the system. If adiabatic potential energy surfaces (APES) are used to describe such interactions, an increased repulsive energy would result in a larger curvature of these energy surfaces [29].

The electronic states of the luminescence centers are related to the positions of the nearby ions, so the form of the optical absorption and emission spectra corresponding to the luminescence center depends on the equilibrium positions and vibrations of these ions [30]. For Tl<sup>+</sup> doped alkali halides, the characteristic emission corresponding

to the  $Tl^+$  center is related to emission spectra excited in the “A-band” (s2 to sp, 1S0 to P1) [28, 29, 31]. Taking the example of NaI(Tl), the emission doublet (Fig. 5) arises from a splitting in the A-band caused by the Jahn-Teller effect. Under this effect,  $Tl^+$  is displaced from the regular lattice site to a more energetically favorable, and therefore, more stable configuration. For NaI(Tl) there are two geometrical distortions—one of which is tetragonal in nature (AT), and the other of which is rhombic (AX) and lower in energy. Each corresponds to a relaxed excited-state minimum on the APES [28-29].

To explain the effect of pressure on Jahn-Teller-split luminescence, Drotning and Drickamer [28] proposed a model based on the co-existence of these two types of minima on the excited state of the APES. For many alkali halides, the application of isostatic pressure results in an increased occupation of the higher-energy state, AT, over the lower-energy one, AX. It is suggested that this phenomenon occurs because the thermal barrier between the states of AT and AX is increased with pressure, thereby hindering the thermal-relaxation path [28]. Thus, as isostatic pressure is applied, emission from AT is preferred over that from AX, and a shift in emission is observed. In the case of CsI(Tl), three emission bands are present, corresponding to three geometrical distortions—tetragonal, orthorhombic, and trigonal in symmetry, and three APES minima [32]. As the applied isostatic pressure is increased, a similar effect occurs in which the heights of the thermal barriers are raised, and the bands convert from one minimum to the next, towards states of greater energy [28].

## 5. Conclusion

The results of this study reveal that the scintillation light output behaves differently for different materials under applied isostatic pressure. Photoluminescence studies were used as an approximation to the scintillation response, and provided the necessary information to explain the observed changes in both scintillation light output as well as scintillation decay times for CsI(Tl), NaI(Tl) and LaBr<sub>3</sub>(Ce). In the case of CsI(Tl), a better matching of the photoluminescence spectrum with the PMT quantum efficiency resulted in the increase in light output collection with applied pressure. Similarly for LaBr<sub>3</sub>(Ce) and NaI(Tl), the decrease in emission intensity of the main emission peak resulted in the decrease in light output.

The scintillation decay times of CsI(Tl) and LaBr<sub>3</sub>(Ce) shortened with applied pressure. In the case of CsI(Tl), this was related to the decrease in the photoluminescence wavelength and an increase of the index of refraction with applied pressure. It was also deduced that other host-charge related interactions occurring in the scintillation interaction are less significant compared to the relaxation behavior of the  $Tl^+$  emission center. For LaBr<sub>3</sub>(Ce), no data was available for the index of refraction as a function of pressure, and the tiny shift in the photoluminescence wavelength could not explain the decrease in decay time of around 10% at 490 MPa.

For the two studied halides, pressure-dependent photoluminescence behavior of the alkali halides was attributed to the effect of pressure on the Jahn-Teller distortion around the  $Tl^+$  site. No existing information has been found on the influence of pressure on the orbital interactions and optical transitions in LaBr<sub>3</sub>(Ce), therefore further study would be needed to elucidate the role of pressure in the emission properties of this material.

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# Characterization of light output and scintillation emission in CsI(Tl), NaI(Tl), and LaBr<sub>3</sub>(Ce) under isostatic pressure

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## ABSTRACT

The application of high isostatic pressure has been known to affect the electronic band structure of the host lattice and the electronic states of luminescence centers in scintillators. Using pulse-height gamma-ray and photoluminescence spectroscopy, the scintillation light output, decay time, and emission behavior of CsI(Tl), NaI(Tl) and LaBr<sub>3</sub>(Ce) were studied under high isostatic pressure up to 800 MPa. The light output behavior of CsI(Tl) was found to exhibit a different trend than those observed by NaI(Tl) and LaBr<sub>3</sub>(Ce), explained by shifts in the photoluminescence wavelengths with increased applied pressure. Scintillation decay times were also observed to shorten with pressure. The observed trends in light output and decay times are explained and compared to estimations by analytical models.

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1 **1. Introduction**

2 Inorganic scintillators are compounds that luminesce when excited  
3 by ionizing radiation. These materials are increasingly used as  
4 radiation detectors in a number of fields, including nuclear medicine,  
5 high energy physics, and homeland security. The ongoing quest for  
6 novel scintillators with improved properties such as light yield, decay  
7 time, energy resolution, and light yield proportionality has stimulated  
8 efforts to more clearly elucidate the relationship between scintillator  
9 performance and a material's structure and chemical composition [1].

10 The application of high isostatic pressure has been shown to affect  
11 a host crystal's electronic band structure as well as the electronic states  
12 of the luminescence centers [2, 3]. Furthermore, band structure  
13 modeling by Setyawan et al. [4] predicts a relationship between light  
14 yield proportionality and applied isostatic pressure. Pressure also  
15 affects the migration and recombination properties of free charge  
16 carriers and excitons [3, 5-8] and hence, light output. The few  
17 published pressure studies to date, however, have been insufficient for  
18 establishing a comprehensive relationship between scintillation  
19 performance and structure. It is clear that more experimental work is  
20 needed to elucidate such a relationship.

21 In this study, the photoluminescence spectra, light output, and  
22 energy resolution of three scintillators, CsI(Tl), LaBr<sub>3</sub>(Ce), and

23 NaI(Tl), were characterized up to isostatic pressures between 600-800  
24 MPa using a custom-designed high-pressure instrument. The decay  
25 times of CsI(Tl) and LaBr<sub>3</sub>(Ce) were also investigated.

26 **2. Experimental setup and methods**

27 CsI(Tl), LaBr<sub>3</sub>(Ce), and NaI(Tl) were characterized in this study  
28 (Table 1). Each 1 cm<sup>3</sup>-sized sample had five ground faces and one  
29 polished face. The samples were wrapped with a specular reflector,  
30 Vikuiti Enhanced Specular Reflective Film (ESR, trademark of 3M),  
31 to optimize the light collection. This was important since the presence  
32 of an optical window prevented direct coupling between the sample  
33 and the photodetector.

34 The pressure instrument consists of an air-driven, two-stage  
35 compressor utilizing heptane as the compression fluid. The pressure

Table 1.  
Structural and luminescence properties for the crystals used in this study.

Crystal	Bulk modulus [GPa]	Emission wavelength [nm]	Light output [ph/MeV]	Decay time [μs]
CsI(Tl)	12.6 [9]	540 [10]	65k [10]	0.8/6 [10]
LaBr <sub>3</sub> (Ce)	N/A	360/380 [11]	60k [11]	0.023 [11]
NaI(Tl)	15.1 [9]	415 [10]	38k [10]	0.23/1 [10]

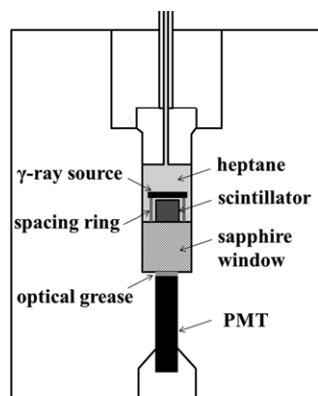


Fig. 1. Scheme of the pressure vessel and associated components. A photomultiplier (PMT) (shown) or optical probe can be coupled to the sapphire window.

1 vessel accommodates samples up to 5 cm<sup>3</sup> in size and is equipped with  
 2 a sapphire optical window. The excitation source, <sup>137</sup>Cs, is placed on  
 3 top of the sample, which sits on the sapphire window (Fig. 1). Details  
 4 about the pressure system and its performance characteristics can be  
 5 found in Gaumc et al. [12].

6 The scintillation light was collected by a Hamamatsu R4141  
 7 photomultiplier tube (PMT) coupled to the exterior of the sapphire  
 8 window with silicone optical grease (Bicron BC-630). A PMT voltage of  
 9 -1 kV was selected as the bias voltage. The output signals were  
 10 amplified with a Canberra 2022 amplifier using shaping times of 4, 0.5  
 11 and 1 μs for CsI(Tl), LaBr<sub>3</sub>(Ce), and NaI(Tl), respectively. The  
 12 selected shaping times were sufficiently long compared to the  
 13 scintillation decay times in the pressure ranges studied. The resultant  
 14 signals were processed with an Amptek MCA-8000 multichannel  
 15 analyzer. A satisfactory signal-to-noise ratio was ensured by collecting  
 16 at least 5,000 to 10,000 counts per photopeak. These were fit using a  
 17 Gaussian function and an exponential background to determine the  
 18 centroid and full-width at half-maximum.

19 For the light output measurements, the system was first pressurized  
 20 up to the maximum pressure, and then held and lowered to a selected  
 21 pressure using a pressure release valve. The relative light output was  
 22 determined by comparing the centroid at a given pressure to its value  
 23 at 0 MPa.

24 The scintillation decay time under <sup>137</sup>Cs excitation was  
 25 characterized at each pressure by recording 1,600 decay traces directly  
 26 from the PMT output using a Yokogawa DL6154 digital oscilloscope  
 27 and a 50 Ω terminator to match the cable impedance. A pulse pile-up  
 28 rejection algorithm was implemented using a ROOT macro  
 29 (<http://root.cern.ch>). The decay traces were fit with double and single  
 30 exponential functions for CsI(Tl) and LaBr<sub>3</sub>(Ce), respectively. The  
 31 scintillation decay time for a given pressure was determined by  
 32 averaging the calculated values derived from the fitted traces.

33 Since the pressure instrument is not compatible with conventional  
 34 x-ray luminescence measurements and the activity of the <sup>137</sup>Cs  
 35 excitation source was low, photoluminescence spectra were collected  
 36 instead of scintillation emission spectra. This was accomplished by  
 37 exciting each sample with monochromatic light, λ<sub>exc</sub> = 300 nm, from  
 38 a 35W Xenon lamp using an Ocean Optics QE 65000 spectrometer  
 39 with a 10 second integration time. Both the excitation and the emission  
 40 were delivered and collected, respectively, using a  
 41 reflection/backscattering optical probe (Ocean Optics, R600-7-  
 42 UV/125F). The excitation wavelength of 300 nm was chosen after  
 43 examining the excitation spectra of CsI(Tl) [13-14], NaI(Tl) [15], and  
 44 LaBr<sub>3</sub>(Ce) [16-17]. At 300 nm, overlap between the excitation and  
 45 photoluminescence spectra was avoided.

46 Due to the hygroscopic nature of NaI(Tl) and LaBr<sub>3</sub>(Ce), these  
 47 samples were stored in anhydrous heptane until transfer into the  
 48 sample chamber of the pressure vessel.

### 49 3. Results

50 The scintillation light output of CsI(Tl), LaBr<sub>3</sub>(Ce), and NaI(Tl)  
 51 under applied pressure are shown in Fig. 2. At 800 MPa, the light  
 52 output of CsI(Tl) increased by 40% while the light output of LaBr<sub>3</sub>(Ce)  
 53 and NaI(Tl) decreased by approximately 15% and 40%, respectively, .

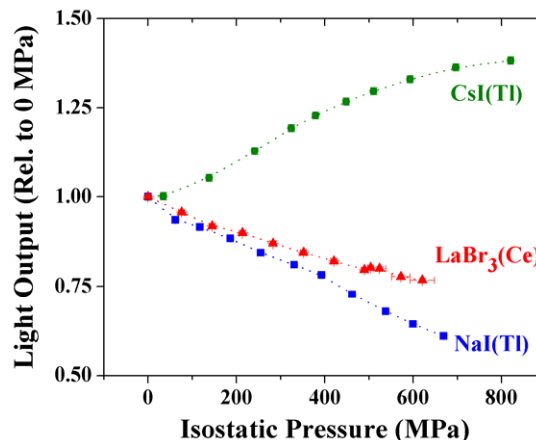


Fig. 2. Light output as a function of isostatic pressure for three different scintillators.

54 The scintillation decay times for CsI(Tl) and LaBr<sub>3</sub>(Ce) were  
 55 determined at regular pressure intervals from 0 to 840 MPa and from 0  
 56 to 497 MPa, respectively. Table 2 shows the measured scintillation  
 57 decay times and intensities for CsI(Tl) and LaBr<sub>3</sub>(Ce). The value in the  
 58 last column of CsI(Tl) corresponds to a fit with one single exponential.  
 59 From Fig. 3, which shows the change in decay time relative to the  
 60 values at ambient pressure, the decay time of CsI(Tl) was observed to  
 61 decrease by 30% of its ambient pressure value. The decay time of  
 62 LaBr<sub>3</sub>(Ce) decreased by less than 10% when pressurized up to 350  
 63 MPa, and remained fairly constant around 23 ns as the applied  
 64 pressure was raised to 500 MPa.

65 The photoluminescence response of CsI(Tl), NaI(Tl), and  
 66 LaBr<sub>3</sub>(Ce) under 300 nm excitation of the Tl<sup>+</sup> and Ce<sup>3+</sup> activator ions  
 67 are shown as a function of pressure in Figs. 4, 5, and 6. At ambient  
 68 pressure, the photoluminescence for CsI(Tl), NaI(Tl), and LaBr<sub>3</sub>(Ce)  
 69 peak around 550 nm (Fig. 4), 340 and 430 nm (Fig. 5), and 355 and  
 70 390 nm (Fig. 6), which is in agreement with the values  
 71 reported in literature [14, 18, 20-21]. The photomultiplier (PMT)'s  
 72 quantum efficiency is also shown on these plots for comparison. The  
 73 arrows indicate the direction of shift in photoluminescence  
 74 wavelengths and change in intensity with applied pressure.

75 Less than 5% degradation in light output was observed after the  
 76 application of isostatic pressure and the scintillation decay times and  
 77 photoluminescence behavior at 0 MPa were also found to be  
 78 reproducible before and after pressurization. Furthermore, no visible  
 79 damage such as cracking or plastic deformation (i.e. dimensional  
 80 changes) was observed in the crystals after applied pressure.

### 81 4. Discussion

82 Initial examination of the variation of light output with pressure for  
 83 CsI(Tl), NaI(Tl) and LaBr<sub>3</sub>(Ce) reveals that CsI(Tl) exhibits a different  
 84 behavior than NaI(Tl), and LaBr<sub>3</sub>(Ce). Since the amount of light  
 85 collected depends on the quantum efficiency of the photomultiplier  
 86 tube, the photoluminescence response for each material was collected  
 87 to verify whether the observed changes in light output were due to  
 88 changes in light output intensity or changes in the overlap between the  
 89 photoluminescence wavelengths and the PMT quantum efficiency.

Table 2.

Measured scintillation decay time constants and intensities for CsI(Tl) and LaBr<sub>3</sub>(Ce) under isostatic pressure. Typical uncertainties are shown on the bottom row.

Pressure (MPa)	CsI(Tl)					LaBr <sub>3</sub> (Ce)	
	I <sub>1</sub>	τ <sub>1</sub> (μs)	I <sub>2</sub>	τ <sub>2</sub> (μs)	Single τ (μs)	Pressure (MPa)	τ (ns)
0	0.76	0.87	0.24	2.5	1.28	0	25.1
140	0.74	0.79	0.26	2.4	1.24	77	24.1
245	0.71	0.67	0.29	2.1	1.17	145	23.7
385	0.54	0.50	0.46	1.6	1.16	217	23.4
455	0.68	0.53	0.32	1.8	1.08	283	23.5
518	0.71	0.51	0.29	1.8	1.03	357	22.8
602	0.71	0.43	0.29	1.6	0.98	427	22.9
700	0.69	0.40	0.28	1.5	0.95	497	22.9
840	0.67	0.41	0.23	1.6	0.9	-	-
± 0.01	± 0.01	± 0.02	± 0.01	± 0.02	± 0.02	± 0.01	± 0.02

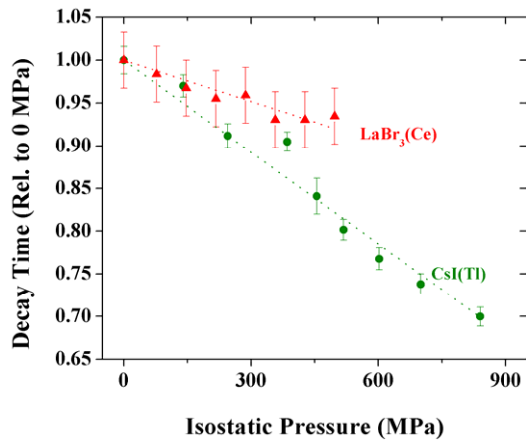


Fig. 3. Scintillation decay time as a function of isostatic pressure for CsI(Tl) and LaBr<sub>3</sub>(Ce).

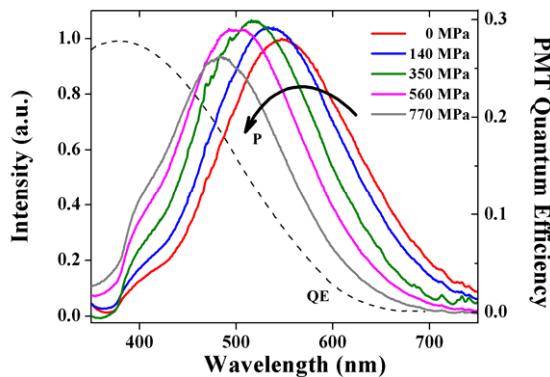


Fig. 4. Photoluminescence response as a function of isostatic pressure for CsI(Tl).

1 From Fig. 4, the blue-shift of the CsI(Tl) photoluminescence  
2 towards regions of higher PMT quantum efficiency has a greater  
3 influence on the light output than the decrease in intensity with  
4 pressure. Consequently, the light output was observed to increase (Fig.  
5 2). For NaI(Tl), the decrease in the 430 nm photoluminescence  
6 intensity offsets the contributions to the light output from the small  
7 blue-shift and the slight increase in the 340 nm intensity. In the case of

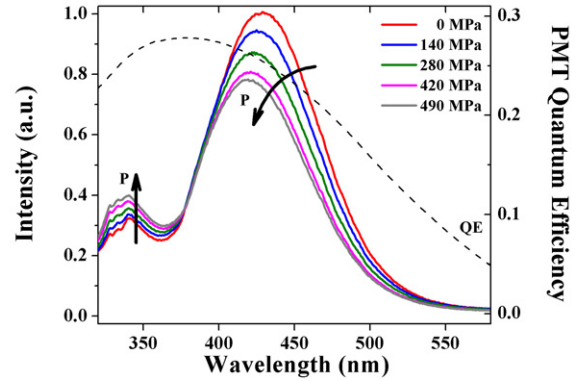


Fig. 5. Photoluminescence response as a function of isostatic pressure for NaI(Tl).

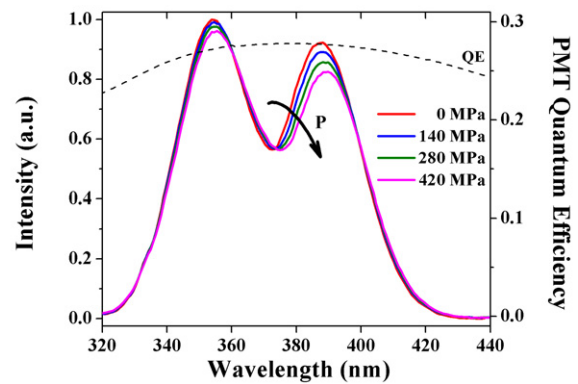


Fig. 6. Photoluminescence response as a function of isostatic pressure for LaBr<sub>3</sub>(Ce).

8 LaBr<sub>3</sub>(Ce), the photoluminescence peaks are centered with respect to  
9 the PMT quantum efficiency. The intensity of the 350 nm peak  
10 remains constant while the intensity of the 380 nm peak decreases,  
11 resulting in a decrease in light output (Fig. 6).

12 For a more quantitative analysis, the scintillation light output can  
13 be compared with the estimated light output, LO<sub>est</sub>, of these  
14 scintillators with pressure using the following formula:

$$15 \quad LO_{est}(P) = \int QE(\lambda) EM(\lambda, P) d\lambda \quad (1)$$

16 where  $QE(\lambda)$  is the PMT quantum efficiency and  $EM(\lambda, P)$  is the  
17 measured emission spectra resulting from gamma-ray excitation. The  
18 result of this convolution can be used to estimate the expected  
19 scintillation light output behavior. The pressure-dependent  
20 photoluminescence spectra (Figs. 4 to 6) were used for  $EM(\lambda, P)$  in  
21 Eqn. (1) since literature shows no significant differences between the  
22 spectra resulting from gamma-ray excitation and those from UV-  
23 excited photoluminescence for CsI(Tl) [13, 20-23], NaI(Tl) [15, 20,  
24 24], and LaBr<sub>3</sub>(Ce) [11, 17, 25] at ambient pressure. Indeed,  
25 comparison of the measured photoluminescence spectra with those in  
26 literature [11, 13, 15, 17, 20-25] for the three materials at 0 MPa (Figs.  
27 4 to 6) confirm that the transitions relevant to the scintillation process  
28 (Tl<sup>+</sup> and Ce<sup>3+</sup> to their respective ground states) were accessed with the  
29 300 nm excitation. Note that while changes in light transmission were  
30 not considered, the estimated light output, LO<sub>est</sub>, in Fig. 7 exhibited  
31 behavior similar to the scintillation light output (Fig. 2). Values fall  
32 within a 15% margin of agreement.

33 The estimated decay times can also be predicted from the peak  
34 centroid of emission  $\lambda_m$ . Yanagida et al. [26] and Dorenbos [16]  
35 showed that in photoluminescence, the decay time can be analytically  
36 deduced as:

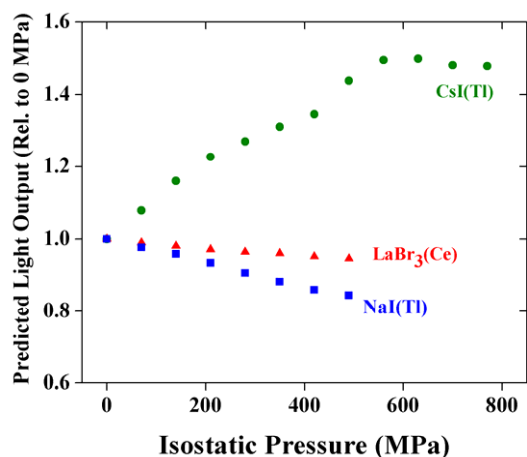


Fig. 7. Estimated light output using Eq. 1 for CsI(Tl), LaBr<sub>3</sub>(Ce), and NaI(Tl).

$$\Gamma = 1/\tau \sim (1/9)(n/\lambda^3)(n^2+2)^2 \sum |<f|\mu|i>|^2 \quad (2)$$

where  $\Gamma$ ,  $\tau$ ,  $n$ , and  $\lambda$  represent the decay rate of an excited state, decay time, refractive index, and photoluminescence wavelengths, respectively.  $|i\rangle$  and  $|f\rangle$  are the initial and final states of the transition and  $\mu$  is the dipole operator. This equation predicts a shorter decay time with a blue shift of emission wavelength and increase of the refractive index. It should be stated that the phenomena of photoluminescence is fundamentally different from that of scintillation. Photoluminescence decay time primarily describes the relaxation time of the emission center, whereas scintillation decay time describes this process in addition to other interactions with the host lattice during the scintillation mechanism such as charge carrier migration. However, a recent study by Yanagida et al. on oxides and fluorides doped with Ce<sup>3+</sup>, Pr<sup>3+</sup>, and Nd<sup>3+</sup> reveals that the differences between the scintillation and photoluminescence decay times are small, and that even in scintillation decay where energy migration occurs from the host lattice to the emission center, the emission process from the excited state of the ground state is dominant [26]. Thus, given this finding, the Eqn. (2) can be used to determine the photoluminescence decay time as an estimation of the scintillation decay time for LaBr<sub>3</sub>(Ce). This equation has also been used to describe the scintillation decay time of LaBr<sub>3</sub>(Ce) elsewhere in [16]. It is less obvious whether Eqn. (2) is also suitable for approximating the scintillation decay time of NaI(Tl) and CsI(Tl) since no comparison studies similar to those of [26] have been performed on these two materials. However, since the scintillation and photoluminescence decay times are 250 and 220 ns for NaI(Tl), respectively, and 700 and 560 ns for CsI(Tl), respectively [20], Eqn. (2) was applied to determine whether the photoluminescence decay would also a good estimate of the scintillation decay.

Since no measurements were available for the pressure-dependent refractive index of LaBr<sub>3</sub>(Ce), the predicted values for this material do not take into account the change in the index of refraction with pressure. The pressure-dependent refractive indices for NaI(Tl) and CsI(Tl) were substituted with those for NaI and CsI measured by Johannsen et al. [27]. Finally, the last term, which is the strength of the transition or the probability of transition, was assumed to be constant for all three materials. Tsujimoto et al. [3] estimated that for CsI(Tl), the last term is not strongly dependent on pressure because the lattice constant is reduced by only 2% at 1 GPa. By applying the same logic for NaI(Tl) and LaBr<sub>3</sub>(Ce), in which even smaller changes in the lattice parameter are expected, the last term was also assumed constant in the analysis for these two materials.

The estimated photoluminescence decay times normalized to ambient pressure are shown in Fig. 8. Despite the

photoluminescence and scintillation decays being comparable at ambient pressure for LaBr<sub>3</sub>(Ce), the two responses deviate with applied isostatic pressure. This is possibly due to unaccounted changes in the refractive index with pressure. On the other hand, for CsI(Tl), the estimated photoluminescence decay response provides a good approximation of the scintillation decay time. We can learn a few interesting things from this latter result for CsI(Tl). Recall from the earlier discussion that photoluminescence and scintillation phenomena are fundamentally different since photoluminescence involves lifetime and relaxation of the emission center, whereas the scintillation decay time includes this process as well as the other interactions with the host lattice and transfer of charge carriers to the emission center during the scintillation mechanism [26]. This is the cause of the difference in measured photoluminescence and scintillation decay times at ambient pressure, as previously mentioned. However, by examining the normalized photoluminescence and scintillation decay responses for CsI(Tl) with applied pressure (Fig. 8), it can be deduced from the similar trends that the evolution of the excited and ground state levels evolve in the same manner with applied pressure, and that other host-charge related interactions occurring in the scintillation interaction are less significant compared to the relaxation behavior of the Tl<sup>+</sup> emission center.

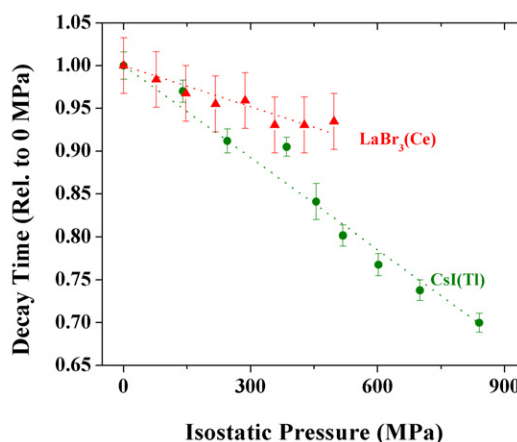


Fig. 8. Normalized photoluminescence decay time as a function of isostatic pressure for CsI(Tl) and LaBr<sub>3</sub>(Ce).

Finally, the overall decrease in both the scintillation and photoluminescence decay times of CsI(Tl) and LaBr<sub>3</sub>(Ce) (Fig. 3) suggest increasing the application of isostatic pressure in our investigated range facilitates the recombination and relaxation process at the emission center. Understanding the precise manner in which this occurs requires further investigation.

In the meantime, however, the scintillation light output and scintillation decay time trends in this study can be related to what is previously known about the emission center and its behavior with applied pressure. While few studies are published regarding the influence of pressure on the emission of LaBr<sub>3</sub>(Ce), the halides have been previously investigated. Firstly, it is well understood that the application of pressure strongly affects the overlap of adjacent orbitals [28]. For example, for the thallium-doped halides, when pressure is applied, the repulsive energy between the thallium and halide ions is increased due to greater orbital overlap between the ions. This modifies the energy states of the system. If adiabatic potential energy surfaces (APES) are used to describe such interactions, an increased repulsive energy would result in a larger curvature of these energy surfaces [29].

The electronic states of the luminescence centers are related to the positions of the nearby ions, so the form of the optical absorption and emission spectra corresponding to the luminescence center depends on the equilibrium positions and vibrations of these ions [30]. For Tl<sup>+</sup> doped alkali halides, the characteristic emission corresponding



to the  $Tl^+$  center is related to emission spectra excited in the “A-band” (s2 to sp, 1S0 to P1) [28, 29, 31]. Taking the example of NaI(Tl), the emission doublet (Fig. 5) arises from a splitting in the A-band caused by the Jahn-Teller effect. Under this effect,  $Tl^+$  is displaced from the regular lattice site to a more energetically favorable, and therefore, more stable configuration. For NaI(Tl) there are two geometrical distortions—one of which is tetragonal in nature (AT), and the other of which is rhombic (AX) and lower in energy. Each corresponds to a relaxed excited-state minimum on the APES [28-29].

To explain the effect of pressure on Jahn-Teller-split luminescence, Drotning and Drickamer [28] proposed a model based on the co-existence of these two types of minima on the excited state of the APES. For many alkali halides, the application of isostatic pressure results in an increased occupation of the higher-energy state, AT, over the lower-energy one, AX. It is suggested that this phenomenon occurs because the thermal barrier between the states of AT and AX is increased with pressure, thereby hindering the thermal-relaxation path [28]. Thus, as isostatic pressure is applied, emission from AT is preferred over that from AX, and a shift in emission is observed. In the case of CsI(Tl), three emission bands are present, corresponding to three geometrical distortions—tetragonal, orthorhombic, and trigonal in symmetry, and three APES minima [32]. As the applied isostatic pressure is increased, a similar effect occurs in which the heights of the thermal barriers are raised, and the bands convert from one minimum to the next, towards states of greater energy [28].

## 5. Conclusion

The results of this study reveal that the scintillation light output behaves differently for different materials under applied isostatic pressure. Photoluminescence studies were used as an approximation to the scintillation response, and provided the necessary information to explain the observed changes in both scintillation light output as well as scintillation decay times for CsI(Tl), NaI(Tl) and LaBr<sub>3</sub>(Ce). In the case of CsI(Tl), a better matching of the photoluminescence spectrum with the PMT quantum efficiency resulted in the increase in light output collection with applied pressure. Similarly for LaBr<sub>3</sub>(Ce) and NaI(Tl), the decrease in emission intensity of the main emission peak resulted in the decrease in light output.

The scintillation decay times of CsI(Tl) and LaBr<sub>3</sub>(Ce) shortened with applied pressure. In the case of CsI(Tl), this was related to the decrease in the photoluminescence wavelength and an increase of the index of refraction with applied pressure. It was also deduced that other host-charge related interactions occurring in the scintillation interaction are less significant compared to the relaxation behavior of the  $Tl^+$  emission center. For LaBr<sub>3</sub>(Ce), no data was available for the index of refraction as a function of pressure, and the tiny shift in the photoluminescence wavelength could not explain the decrease in decay time of around 10% at 490 MPa.

For the two studied halides, pressure-dependent photoluminescence behavior of the alkali halides was attributed to the effect of pressure on the Jahn-Teller distortion around the  $Tl^+$  site. No existing information has been found on the influence of pressure on the orbital interactions and optical transitions in LaBr<sub>3</sub>(Ce), therefore further study would be needed to elucidate the role of pressure in the emission properties of this material.

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