Experimental and theoretical studies of donor–acceptor scintillation from PbI₂

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ABSTRACT

We report on the scintillation properties of undoped PbI₂ and PbI₂ doped with La, Cu, Ag, and Te. X-ray luminescence spectra were recorded at 7 K and the time responses for 80 ps pulses of X-rays were recorded from 14 K to 150 K. Samples were irregularly shaped crystal pieces that ranged from 300 to 1000 μm in size. We found that at 14 K the undoped samples had a fast emission at 520 nm (0.18 eV below the band edge) and a total light output of about 40,000 photons/MeV. 10% of this light appears in the first ns, which is 5 times greater than LSO and 1.5 times greater than LaBr₃:Ce. 50% of the light appears in the first 100 ns. The luminosity decreased dramatically as the temperature was increased above 40 K, consistent with a non-radiative path that has an activation energy of 3.8 meV. Doping with the donor La³⁺ only slightly changed these scintillation properties. Doping with the donor La³⁺ and the deep acceptors Cu⁺, Ag⁺, and Te⁺ produced primarily slow donor–acceptor emissions at peak wavelengths of 605, 653, and 800 nm, respectively. The luminosity of the samples doped with La³⁺ and Cu⁺ depended strongly on the La³⁺ concentration, demonstrating its role as an electron donor. First-principles band structure calculations showed (1) that the donor level depth of an isolated iodine vacancy is about 0.8 eV, too deep to explain the 520 nm emission wavelength, and (2) that a donor–acceptor pair consisting of a spatially associated iodine vacancy donor and a lead vacancy acceptor has shallower donor and acceptor depths that are consistent with the 520 nm emission wavelength.

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1. Introduction

Ultra-fast scintillation has been observed from several semiconductors, including ZnO, CdS, PbI₂, HgI₂, and CuL₁ [1–8]. In these materials ionization electrons on shallow donor sites rapidly recombine with ionization holes trapped on either acceptors or isoelectronic impurities. It is interesting to note that possibly the brightest known scintillator ZnS(Ag,Cl) is also donor–acceptor bound exciton radiative transitions in cryogenic temperatures but we did not identify the donors or acceptors involved [4].

In this paper we report on the scintillation properties of larger (300 to 1000 μm) pieces of polycrystalline PbI₂ that were undoped, and that were doped with La, Cu, Ag, and Te. This allowed a better estimate of the absolute luminosity (in photons/MeV) and measurements of donor and acceptor ionization energies. We also describe the results of first-principle calculations and discuss the possible donors and acceptors that are responsible for the fast scintillation from undoped PbI₂, the slower scintillation from impurity donors and acceptors, and the dramatic decrease in luminosity as the temperature is increased above 40 K.

2. Background

PbI₂ has a rhombohedral crystal structure with a=b=0.456 nm, c=0.698 nm, α=90°, β=90°, and γ=120°. The space group is P-3 m1, no. 164. The density is 6.16 g/ml, the melting point is 402 °C, and it is stable under normal atmospheric conditions. It is a direct-gap semiconductor with a band gap of 2.531 eV at 4 K that decreases at about 1.0 meV/K [12]. At 4 K the free exciton emission is at 2.498 eV, the dominant bound exciton emission is at 2.493 eV, and a broader donor–acceptor emission complex is centered at 2.45 eV [13]. Other works report a band gap of 2.58 eV and a free exciton emission energy of 2.51 eV [14]; and a free
exciton emission energy of 2.518 eV and a defect-bound exciton emission energy of 2.506 eV [15].

The crystal consists of repeated I-Pb-I planes where the facing I planes are bonded by Van der Waals forces. Several polytypes are possible, the most common being 2H. Crystals of cm size have been grown and characterized as semiconductor radiation detector materials [16–18].

Undoped PbI2 at room temperature is p-type with a reported resistivity ranging from $2 \times 10^8$ Ω-cm [19] to $10^{11}$ Ω-cm [20] to $10^{12}$ Ω-cm [12,21]. Thermal conductivity measurements were used to measure a hole concentration of 4.84 $\times$ 10$^{11}$ cm$^{-3}$ [22]. The low-temperature emissions near 2.45 eV have been ascribed to donor–acceptor recombinations between two shallow native donors (20 meV and 28 meV from the conduction band minimum) and a native acceptor (72 meV from the valence band maximum) [23]. The same paper speculates that it is most likely that the two native donors are an iodine vacancy and an interstitial lead, and that the native acceptor is a lead vacancy.

Thermally stimulated current measurements detected a dominant hole trap 0.59 eV from the valence band maximum, which was tentatively attributed to a Pb vacancy [19]. Optically detected magnetic resonance data suggest that this hole trap is a doubly charged lead vacancy acceptor (singly charged after capturing a hole) and non-radiative, and that the singly charged lead vacancy acceptor (neutral after trapping a hole) is radiative [24].

The importance of iodine vacancies in the emissions near 520 nm was demonstrated by annealing samples in iodine and observing a significant decrease in those emissions [7].

Doping with Cu$^+$ and Ag$^+$ was reported to introduce deep acceptors with emissions in the 600 nm and 650 nm regions, respectively [25,26].

3. Materials and methods

3.1. Materials

Commercial PbI2 with a purity of 99.999% and selected dopants were mixed in powder form, melted by heating to 450 °C, mixed, and solidified. The polycrystalline mass was gently separated with a ceramic knife to produce irregular crystal pieces that ranged from 300 to 1000 μm. The Lu2SiO5:Ce reference sample was sieved for 800 ± 200 μm particle size. The LaBr3:Ce reference sample was sieved for 780 ± 70 μm particle size.

In a previous study [27] we ground single crystals of Bi4Ge3O12, Lu2SiO5:Ce, LaBr3:Ce, and YAlO3:Ce, sieved them to produce samples whose particle sizes ranged from 20 μm to 2000 μm, and measured their luminosities in our X-ray luminescence spectrometer (50 keVp) and our pulsed x-ray facility (30 keVp) [28]. We found that the apparent luminosity decreased with decreasing particle sizes below 100 μm as increasing optical scattering reduced the collection efficiency of the scintillation photons produced at the distal end of the X-ray penetration profile. For particles above 1000 μm the apparent luminosity decreased due to the decreasing packing fraction of the particles in our sample cuvettes which had an inner diameter of 3 mm. However for particles in the 300–800 μm range the ratio of apparent luminosity to published luminosity values was constant to within 20% and this size range was used in this work.

3.2. X-ray luminosity

Samples in fused silica cuvettes were loaded into a cryostat and exposed to continuous 50 keVp white X-rays and their emission spectra and intensity was measured in the system described in Ref. [28]. Luminous intensities were calibrated using room temperature samples of Lu2SiO5:Ce and LaBr3:Ce of similar crystal particle size [27].

3.3. Pulsed X-ray

Samples in fused silica cuvettes were loaded into a cryostat and exposed to 80 ps pulses of 30 keVp white X-rays produced by a light-excited X-ray tube at a repetition rate of 150 kHz. Scintillation photons were recorded using a Hamamatsu R3809U-50 microchannel PMT. This system is described in Refs. [29,30]. Decay time curves and luminous intensities were measured using room temperature samples of Lu2SiO5:Ce and LaBr3:Ce of similar crystal particle size [27]. The system impulse response was determined by sending the pulsed X-rays onto a 1 mm thick crystal of PbF2, painted black on five sides. The photogenerated in the PbF2 crystal generate a bremsstrahlung spectrum that extends down to photon energies that can be detected by the microchannel PMT [31]. The system impulse response has a full-width at half-maximum of 230 ps. Selection of wavelength bands was done with interference filters (Oriel Instruments, Stratford, CT).

3.4. First-principles calculations

Our theoretical calculations are based on density functional theory (DFT) in the generalized gradient approximation (GGA) with the functional of Perdew, Burke, and Ernzerhof (PBE) [32] for the exchange correlation potential, as implemented in the VASP program (Vienna ab-initio simulation package) [33–35]. Projector augmented wave (PAW) pseudopotentials are used to model the interaction of the valence electrons with the core electrons [36].

Our calculation procedure is to take the atomic positions and crystal symmetry group information of PbI2 from the Inorganic Crystal Structure Database (ICSD) [37]. From the three-atom unit cell we then construct a large supercell (typically 54 atoms in most simulations) by repeating the primitive unit cell along the crystal axes. We then introduced the dopant or defect into the system and allowed all the atoms to relax but kept the cell geometry and dimensions fixed. We then performed a ground-state calculation for the final relaxed system and determined the partial projected density of states (DOS) for this system showing the position of the dopant or defect states within the gap of the host material. The plane wave basis set for the electronic wave functions was defined by a cutoff energy of 175.6 eV. Integration within the Brillouin zone was performed on a gamma-centered $2 \times 2 \times 2$ grid of k-points. The total energy convergence criterion was set to $10^{-6}$ eV. Structural relaxations of atomic positions were carried out until the residual forces on all atoms were less than 0.01 eV/Å.

4. Results

4.1. Measurements of undoped PbI2

Fig. 1 shows the emission spectrum when an undoped sample at 7 K was exposed to a constant beam of 50 keV X-rays. It consists of a dominant peak near 520 nm as reported earlier [23] plus emissions at longer wavelengths.

Table 1 lists the scintillation properties at four different temperatures and shows a dramatic drop in luminosity above 40 K. The emission energy at 14 K is 2.371 eV, 0.18 eV below the band edge, and decreases at about 0.15 meV/K.

With pulsed X-ray excitation the emission time spectra cannot be described by a single exponential decay time. Table 2 lists the time required to receive specific fractions of the light at four different wavelengths using interference filters described by their
The dramatic increase in times with wavelength is expected from donor–acceptor emission and rules out emission from a single radiative center. Table 3 lists the fractions of light received after specific times at four different temperatures. Unlike the data in Table 2, filtering was not used and these fractions include the slower light from wavelengths longer than 540 nm (Fig. 1) detected by the microchannel phototube. For comparison with Table 3, Table 4 lists the decay fractions for Lu$_2$SiO$_5$:Ce (LSO) at room temperature after the same time. LSO has nearly identical scintillation properties below room temperature and is almost always used at room temperature. It can be seen that the amount of light emitted in the first ns for PbI$_2$ at 14 K is 4.5 times larger than that of LSO. The rise time of the undoped PbI$_2$ emission is less than 200 ps at all temperatures studied.

Fig. 3 shows an Arrhenius plot of the fraction lost to the non-radiative path. When 1/kT < 0.1 (T > 120 K), essentially all the light is lost. At lower temperatures the fraction lost decreases with a slope that corresponds to an activation energy of 3.8 ± 0.3 meV. The error bars were determined by propagating the standard deviations of repeated measurements.

### 4.2. Measurements of PbI$_2$(La)

Fig. 4 shows the emission spectrum when a sample doped with 0.5% metallic lanthanum at 7 K was exposed to a constant beam of 50 keVp X-rays. The peak emission energy is at 2.388 eV (0.016 eV higher than the undoped sample). First-principles calculations show that the compensating donor electron is near the bottom of the conduction band and localized on the La$^{3+}$ ion. The electrical resistivity of a 1 mm thick layer of powder pressed between two titanium anvils [38] was greater than 1 GΩ. The addition of lanthanum decreased the emission at wavelengths above the 520 nm peak.

Fig. 5 shows the time response of the emissions with pulsed X-ray excitation. At low temperatures the peak intensity is 6 times higher than that of Lu$_2$SiO$_5$:Ce and 1.6 times higher than that of LaBr$_3$:Ce.
Table 5 lists the scintillation properties at four different temperatures and shows a dramatic drop in luminosity above 40 K. The emission energy at 14 K is 2.388 eV, 0.17 eV below the band edge, and decreases at about 0.15 meV/K.

Table 6 lists the fraction of light received after specific times. It can be seen that the amount of light emitted in the first ns for PbI₂ at 14 K is 4.1 times larger than that of LSO. The rise time of the emission is less than 200 ps.

4.3. Measurements of PbI₂ doped with La and Cu, Ag, or Te

With the addition of 0.2% Cu⁺ to the 0.2% La-doped material, the luminosity is much slower, and the emission wavelength peaks at 600 nm. The Cu⁺ acceptor is 0.5 eV deeper than the native acceptor. The absence of any 520 nm emissions indicates that Cu⁺ introduces an acceptor level that is able to trap holes with much higher efficiency than the native acceptors. However, the overlap of the Cu⁺ trapped holes and the La³⁺ compensating donor electrons is poor, resulting in low luminosity at low La³⁺ concentrations (Fig. 6, Table 7). As the La concentration increases to 1% and 3%, the luminosity increases significantly. This is evidence of an increase in donor electron concentration and a corresponding increase in electron–hole spatial overlap. However, even at the highest La³⁺ concentrations the decay remains slow (Figs. 7 and 8).

Fig. 9 shows the emission spectrum of PbI₂ doped with the donor 0.05% La and the acceptor 0.2% Ag at 10 K. Some emission

Table 5
Scintillation properties of PbI₂ (0.5% La) vs. temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>λ_peak (nm)</th>
<th>E_peak (eV)</th>
<th>Total luminositya</th>
<th>Peak luminosityb</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>519.2</td>
<td>2.388</td>
<td>1.5</td>
<td>6.1</td>
</tr>
<tr>
<td>40</td>
<td>520.5</td>
<td>2.382</td>
<td>0.7</td>
<td>4.4</td>
</tr>
<tr>
<td>77</td>
<td>523.2</td>
<td>2.370</td>
<td>0.16</td>
<td>2.0</td>
</tr>
<tr>
<td>150</td>
<td>524.9</td>
<td>2.362</td>
<td>0.006</td>
<td>0.2</td>
</tr>
</tbody>
</table>

a Relative to Lu₂SiO₅:Ce.
b After 80 ps X-ray pulses, relative to Lu₂SiO₅:Ce.

Table 6
Decay time fractions PbI₂ (0.5% La).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>First 1 ns</th>
<th>First 3 ns</th>
<th>First 10 ns</th>
<th>First 30 ns</th>
<th>First 100 ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.09</td>
<td>0.22</td>
<td>0.35</td>
<td>0.44</td>
<td>0.50</td>
</tr>
<tr>
<td>40</td>
<td>0.13</td>
<td>0.32</td>
<td>0.53</td>
<td>0.66</td>
<td>0.75</td>
</tr>
<tr>
<td>77</td>
<td>0.29</td>
<td>0.59</td>
<td>0.80</td>
<td>0.86</td>
<td>0.89</td>
</tr>
<tr>
<td>150</td>
<td>0.57</td>
<td>0.75</td>
<td>0.79</td>
<td>0.80</td>
<td>0.82</td>
</tr>
</tbody>
</table>

a Relative to Lu₂SiO₅:Ce.

Table 7
Scintillation properties of PbI₂ (La, 0.2% Cu).

<table>
<thead>
<tr>
<th>La concentration (%)</th>
<th>Temperature (K)</th>
<th>λ_peak (nm)</th>
<th>E_peak (eV)</th>
<th>Total luminositya</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>14</td>
<td>605.2</td>
<td>2.049</td>
<td>0.118</td>
</tr>
<tr>
<td>0.2</td>
<td>77</td>
<td>606.5</td>
<td>2.044</td>
<td>0.063</td>
</tr>
<tr>
<td>1</td>
<td>14</td>
<td>599.3</td>
<td>2.069</td>
<td>0.69</td>
</tr>
<tr>
<td>1</td>
<td>77</td>
<td>602.9</td>
<td>2.057</td>
<td>0.19</td>
</tr>
<tr>
<td>3</td>
<td>14</td>
<td>596.5</td>
<td>2.079</td>
<td>1.18</td>
</tr>
<tr>
<td>3</td>
<td>77</td>
<td>599.4</td>
<td>2.069</td>
<td>0.31</td>
</tr>
</tbody>
</table>

a Relative to Lu₂SiO₅:Ce.

Fig. 4. Emission spectrum of PbI₂ doped with 0.5% La recorded at 7 K.

Fig. 5. Initial intensity of 0.5% lanthanum-doped PbI₂ at different temperatures compared with Lu₂SiO₅:Ce and LaBr₃:Ce.

Fig. 6. Emission spectra for PbI₂ doped with 0.2% Cu⁺ and three La³⁺ concentrations recorded at 7 K.

Fig. 7. Emission time spectra for PbI₂ doped with 0.2% Cu⁺ and three La³⁺ concentrations recorded at 14 K.
at 520 nm is seen because at this Ag concentration some native acceptors also contribute to the emissions.

Fig. 10 shows the emission spectrum of PbI$_2$ doped with 0.5% La and 0.75% Te. The emissions are above 700 nm, and show that Te$_2^-$ is a deep acceptor.

Table 8 summarizes the measured photon emission energies for Cu$^+$, Ag$^+$ and Te$_2^-$ and their acceptor depths.

Table 8

<table>
<thead>
<tr>
<th>Donor Acceptor</th>
<th>Emission peak (eV)</th>
<th>Acceptor depth (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$ (0.2%)</td>
<td>Cu$^+$ (0.2%)</td>
<td>605 (2.05)</td>
</tr>
<tr>
<td>La$^{2+}$ (1.0%)</td>
<td>Ag$^+$ (0.5%)</td>
<td>653 (1.90)</td>
</tr>
<tr>
<td>La$^{3+}$ (0.5%)</td>
<td>Te$_2^-$ (0.75%)</td>
<td>802 (1.55)</td>
</tr>
</tbody>
</table>

at 520 nm is seen because at this Ag concentration some native acceptors also contribute to the emissions.

Fig. 10 shows the emission spectrum of PbI$_2$ doped with 0.5% La and 0.75% Te. The emissions are above 700 nm, and show that Te$_2^-$ is a deep acceptor.

Table 8 summarizes the measured photon emission energies for Cu$^+$, Ag$^+$ and Te$_2^-$ and their acceptor depths.

5. Theory

Fig. 11 shows the total density of states (DOS) plot for undoped, defect-free PbI$_2$. Vertical line shows the Fermi level (set to 0 eV). The top of the valence band has I 5p character, and the bottom of the conduction band has Pb 6s character.

Fig. 12 shows the total density of states plot for an isolated occupied iodine vacancy in PbI$_2$. The electron centered on the vacancy has an energy about 0.8 eV below the conduction band minimum.

Fig. 12 is the total DOS plot for PbI$_2$ with an isolated occupied iodine vacancy and shows that the electron trapped at the vacancy is about 0.8 eV below the conduction band. This is understandable because an electron in an anion vacancy experiences a coulomb binding similar to the Madelung potential of the anion that it replaced. It can be compared with the electron trapping energies on F centers in alkali halides [39–41] and semiconductors [42] and is not consistent with the very shallow native donor depths reported in PbI$_2$ [23].

One way to reduce the binding energy of the electron is to introduce a nearby repulsive agent, such as a charged lead vacancy.

Fig. 13 is the total DOS plot for PbI$_2$ with a neutral lead vacancy. The highest occupied state (the Fermi level) is at 0 eV. The empty localized acceptor states associated with the lead vacancy are near the top of the valence band.

Since PbI$_2$ is weakly p-type at room temperature, there are unoccupied acceptor states and an iodine vacancy will also be unoccupied and will have a net charge of plus 1. Since it is known that iodine vacancies can migrate to oppositely charged defects, including K$^+$ ions and lead vacancies [43], it is plausible that ionized iodine vacancies will form complexes with charged lead vacancies.

Fig. 14 shows the total DOS plot for a neutral vacancy pair complex where the iodine vacancy has an unoccupied donor state and a charge of plus one and the lead vacancy has one unoccupied acceptor state and a net charge of minus one. It is seen that the donor state in this vacancy pair system is much shallower than it
increasing temperature as shown in Figs. 2 and 5. If the excited states after their formation. This is evidenced by the number of excited states, rather than to the thermal quenching of raised to 150 K. Most of this decrease is due to the decrease in the intensity five times larger. However, the total luminosity decreases by a factor greater than 200 as the temperature is decreased by a factor greater than 200 as the temperature is increased to 150 K. Most of this decrease is due to the decrease in the intensity five times larger.

The acceptor-state energy associated with the lead vacancy has moved from a mid-gap position (Fig. 12) to just below the conduction band minimum.

is in the isolated iodine vacancy (Fig. 12), and that the lead vacancy acceptor is also shallow. Spatial plots of the states just below the bottom of the conduction band showed them to be shallow donor states localized on the iodine vacancy. The combined depths (< 200 meV) are consistent with the near band-edge emission near 520 nm described in the previous section. More details of these theoretical results will be published in a future paper.

6. Discussion

6.1. Undoped PbI$_2$

Undoped PbI$_2$ at 14 K is a remarkably bright ultra-fast scintillator with a luminosity similar to that of Lu$_2$SiO$_5$:Ce and an initial intensity five times larger. However, the total luminosity decreases by a factor greater than 200 as the temperature is raised to 150 K. Most of this decrease is due to the decrease in the number of excited states, rather than to the thermal quenching of the excited states after their formation. This is evidenced by the nearly time-independent decrease in the decay curves with increasing temperature as shown in Figs. 2 and 5. If the excited states were thermally quenched then increasing temperature would have the least effect at early times and would decrease the luminosity by progressively larger amounts at later times. One possible explanation is that there is a non-radiative path with a thermal activation energy of about 4 meV (Fig. 3) and that this corresponds to the binding energy of the exciton with some defect. This is in agreement with previous optical measurements that show emissions from a defect bound exciton 5.5 meV lower than the emissions from the free exciton.

In previous reports the donor has been associated with an iodine vacancy and the acceptor has been associated with a lead vacancy [23,24] but an isolated iodine vacancy donor is too deep (Fig. 12) to produce the near band-edge emission as shown in Figs. 1 and 4. For example, the F-center electron is 1.4 eV below the conduction band in CdTe [42] and 2.9 eV below in ZnS [44]. We suggest that an ionized iodine vacancy donor (charge plus 1) paired with a singly charged lead vacancy (charge minus 1) forms a shallow neutral donor-acceptor pair as seen in the calculated total DOS plot (Fig. 14) and is a possible candidate for the radiative center in our samples. Similar correlated donor-acceptor pairs have been seen in other systems [45–47].

In this work we are unable to determine the identity of the exciton binding center but due to the observed rapid rise time, the simplest explanation is that the donor-acceptor vacancy pair acts both as the exciton binding center and as the radiative center. However, we cannot rule out the possibility that the exciton binding center is some other defect that is able to quickly transfer its energy to the donor-acceptor radiative center. We were able to determine the identity of the non-radiative centers.

6.2. La doped PbI$_2$

In this work doping PbI$_2$ with metallic lanthanum made very little difference in the scintillation properties, except for a slight increase in the scintillation photon energy. Apparently lanthanum provides donor electrons that are sufficiently bound so that they do not interfere with the processes described in the previous section for undoped PbI$_2$.

6.3. La, Cu doped PbI$_2$

By adding the acceptor Cu$^+$ to the lanthanum-doped PbI$_2$ the emission spectrum changed dramatically. The emission photon energy decreased by about 0.30 eV, the luminosity depended strongly on the La$^{3+}$ concentration, and the decay time became much longer. In this case the Cu$^+$ is such an efficient hole trap
that all the emission results from a transition between the La$^{3+}$ donor to the deep Cu$^{+}$ acceptor and the emission at 520 nm is not observed.

7. Conclusions

Pbl$_2$ is a moderately bright, fast scintillator, but only at cryogenic temperatures. The fast emission peaks at 520 nm, 0.18 eV from the band edge, and has the characteristics of recombination between shallow donors and acceptors. For both the undoped and La$^{3+}$ doped samples, the scintillation luminosity decreased sharply as the temperature was increased above 40 K. This is consistent with a process that prevents the formation of the excited state, has an energy barrier of about 4 meV, and results in non-radiative quenching.

Co-doping Pbl$_2$ with La$^{3+}$ donors and with Cu$^+$, Ag$^+$ and Te$^{2–}$ acceptors resulted in slow scintillation emissions. Ionization electrons and holes are captured by the nearest donor and acceptor, respectively, resulting in large average separation distances, poor overlap, and long decay times.

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