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## Exciton 4.29 and 3.65 eV luminescence in CsI:Tl and CsI:Pb

S Zazubovich<sup>†</sup>, R Aceves<sup>‡</sup>, M Barboza Flores<sup>‡</sup>, P Fabeni<sup>§</sup>, T Kärner<sup>†</sup>,  
G P Pazzi<sup>§</sup>, R Perez Salas<sup>‡</sup> and N Jaanson<sup>†</sup>

<sup>†</sup> Institute of Physics, Riia Street 142, EE2400 Tartu, Estonia

<sup>‡</sup> CIFUS, Universidad de Sonora, 83190 Hermosillo, Sonora, Mexico

<sup>§</sup> Institute of Electromagnetic Waves of CNR, 50127 Florence, Italy

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**Abstract.** The 4.29 and 3.65 eV emission of CsI:Pb crystals has been studied at 4.2–300 K under excitation in the exciton as well as in the lead-induced absorption bands. The results have been compared with those obtained for the corresponding emission of CsI:Tl as well as for the emission of the on-centre and the off-centre self-trapped exciton in a pure CsI crystal. It has been found that, unlike the case in CsI:Tl, in CsI:Pb the 4.29 and 3.65 eV emission is excited not only in the exciton bands but also in the absorption bands of electron impurity centres optically created at 4.2 K together with the  $V_K$  centres by photons of 5.1–4.0 eV energy. In the latter case this emission is of  $\{e^- + V_K\}$  nature. The optical creation of the  $V_K$  centres has been confirmed by luminescence polarization and ESR spectrum measurements.

### 1. Introduction

The detailed study of luminescence carried out in a wide temperature range down to 0.4 K by time-resolved polarization spectroscopy methods has allowed us to conclude that the intense visible emission of Tl<sup>+</sup>-doped caesium halides is caused by the radiative decay of an exciton perturbed by the Tl<sup>+</sup> ion [1–4]. Based on these results, a new model of the relaxed excited state (RES) structure has been proposed in [1], where the coexistence of the Tl<sup>+</sup>-like trigonal and tetragonal Jahn–Teller minima and the Tl<sup>+</sup>-perturbed exciton states is suggested in the RES of the luminescence centre.

One may assume that the peculiarities of the RES structure found for CsX:Tl (X = halogen) crystals may also be the characteristics of caesium halides doped with some other ‘heavy’  $ns^2$  ions (Pb<sup>2+</sup>, Bi<sup>3+</sup>). It may be expected that some of these systems could also be used as effective scintillators. Some preliminary data obtained in the luminescence study of CsX:Pb crystals have been reported in [5]. In the present paper, the ultraviolet 4.29 and 3.65 eV emission of CsI:Pb is studied in detail and compared with the analogous emission in CsI:Tl and in a pure CsI crystal.

### 2. Experimental procedure

Single crystals of CsI:Pb were grown by the Stockbarger method in vacuum from the zone refined CsI salt. Two crystals of different origin and with different Pb<sup>2+</sup> concentrations (250 ppm in the melt, grown in Prague by K Nitsch, and 100 ppm in the melt, grown in

Tartu) were studied. The samples were cut parallel to the (100) planes of the crystal and polished. Before each measurement the sample was quenched by rapid cooling to room temperature or to liquid nitrogen temperature after heating for 30 min at 550 °C.

The spectral and polarization measurements were carried out with the computer-controlled spectrometer Fluoromax (Spex) as well as with the use of the set-up and experimental procedure described in [2] and [6]. The polarization of the emission was detected in the [010] direction perpendicular to the [100] direction of the excitation light. The polarization degree was defined as

$$P = (I_{[001]} - I_{[100]}) / (I_{[001]} + I_{[100]})$$

where  $I_{[001]}$  and  $I_{[100]}$  are the intensities of the emission polarized along the [001] and [100] directions, respectively. The ESR spectra were recorded by an X-band ERS-231 spectrometer equipped with an Oxford Instruments helium continuous-flow cryostat ESR 900A.

### 3. Experimental results

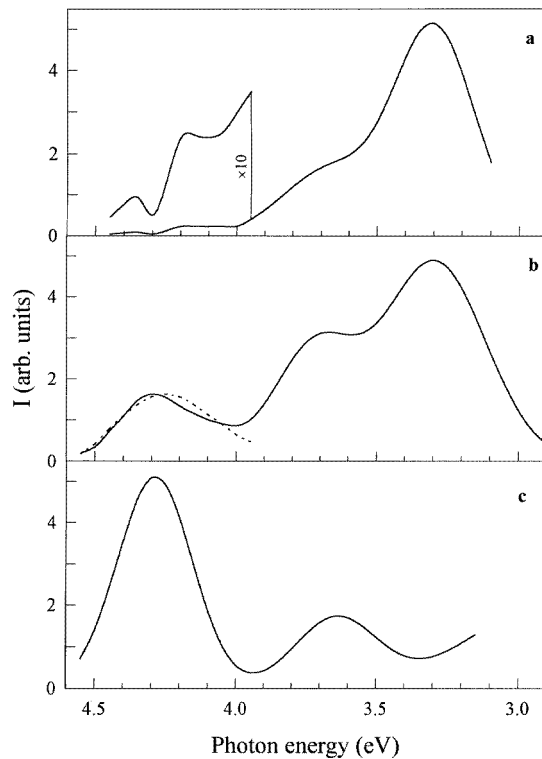
#### 3.1. Emission spectra

In the emission spectrum of CsI:Tl, apart from the two ultraviolet (3.35 and 3.09 eV) and two visible (2.55 and 2.25 eV) emission bands of the thallium centre which have been studied and interpreted in [1–4], two additional weak bands peaking near 4.3 and 3.65 eV and resembling the on-centre and the off-centre self-trapped exciton (STE) emission in pure CsI (see, e.g. [7–14]) are observed at 4.2 K under excitation in the exciton absorption bands (figure 1(a)). The shape of the  $\approx 4.3$  eV band is strongly perturbed due to the reabsorption in the A absorption band of Tl<sup>+</sup> centres. In the samples studied this band is considerably weaker than the 3.65 eV band.

In the emission spectrum of CsI:Pb, besides several bands peaking in the spectral range of 3.3–2.1 eV, the 4.29 and 3.65 eV bands are also observed at 4.2 K (figure 1(b) and (c)). In a non-illuminated CsI:Pb crystal they can be excited only within the exciton absorption region (6.2–5.8 eV). Under excitation in the lower-energy ( $E < 5.8$  eV) lead-induced absorption bands their intensity is negligible. In the process of crystal illumination at 4.2 K by photons of 5.1–4.0 eV energy, the intensities of both the 4.29 and 3.65 eV emission bands increase in parallel, reaching saturation after 1–3 h illumination (figure 2(a)). The  $I(t)$  curve depends on lead concentration and sample quenching conditions. With illumination in the exciton absorption bands (figure 2(b)), as well as in the 3.7–3.5 eV region, their intensities do not change. The intensities of the lead-induced 3.1, 2.6 and 2.3 eV emission bands [5] do not decrease in the process of illumination.

Under excitation at 4.2 K in the exciton bands (6.2–5.8 eV) the 3.65 eV emission is more intense than the 4.29 eV emission (figure 1(b)). Under excitation in the lead-induced 5.8–3.4 eV bands the 4.29 eV emission is about three times as intense as the 3.65 eV emission (figure 1(c)). This intensity ratio remains constant at any excitation in the 5.8–3.4 eV energy range and does not change during the illumination. Such an intensity ratio is characteristic of the recombination  $\{e^- + V_K\}$  luminescence [11].

Some additional weak bands are observed in the emission spectra of both of the crystals studied. Their characteristics and origin will be considered in a separate paper. The most intense of them peak near 3 eV (excited at 5.5–5.4 eV) and near 3.3 eV (excited at 5.8–5.7 eV). Under 5.78–5.42 eV excitation a weak 4.25 eV emission is detected as well. Some of these bands may arise from excitons perturbed by defects (e.g., Na<sup>+</sup>, K<sup>+</sup>; see [7]). In the



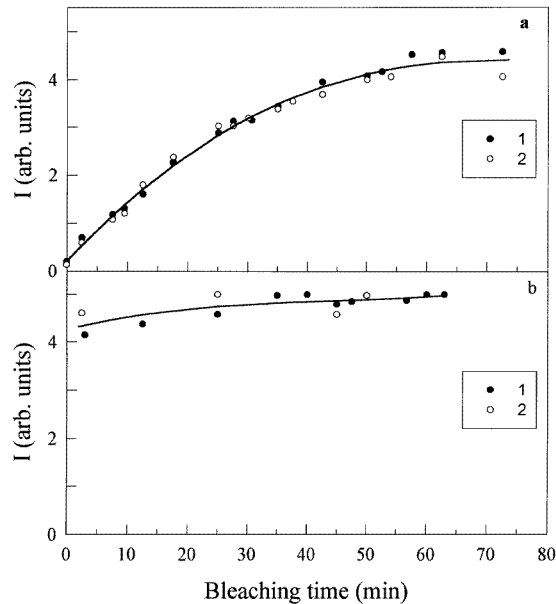
**Figure 1.** Emission spectra of (a) CsI:Tl and (b, c) CsI:Pb measured at 4.2 K under excitation (a, b) in the exciton bands and (c) in the optically created lead-induced absorption bands. The dotted curve in (b) is obtained under 5.75–5.4 eV excitation.

excitation spectrum of the other exciton-like emissions (e.g. the 2.55 and 2.25 eV emissions of CsI:Tl) the 5.5–5.4 eV band is absent.

### 3.2. Excitation spectra

The excitation spectrum of the 4.29 and 3.65 eV emissions in CsI:Tl and in a quenched CsI:Pb crystal (without preillumination) consists of several narrow bands peaking at 6.15–6.05, 5.97, 5.9 and 5.82 eV (see curves 1 and 2 in figure 3). Their maxima coincide for the two emissions, and they are characteristic of the STE emission in CsI. The 4.29 eV emission (curve 1) is more effectively excited in the higher-energy region (6.15–5.90 eV), while the 3.65 eV emission (curve 2) is more effectively excited in the lower-energy (5.82 eV) band. The 4.29 and 3.65 eV emissions are not excited in the thallium-induced absorption bands. Without preillumination of the CsI:Pb crystal they are not excitable in the lead-induced bands either. Strongly overlapping bands in the 5.8–3.4 eV energy range appear only as a result of the illumination of the CsI:Pb crystal at 4.2 K by photons of 5.1–4.0 eV energy (figure 3(b) and (c), curves 1' and 2'). The excitation spectra may be perturbed by the impurity absorption bands peaking at 3.72, 4.05 eV, etc. In the process of illumination the intensities of all lead-induced excitation bands increase in parallel, but the intensities of all the exciton bands remain unchanged.

Thus, unlike the case of CsI:Tl, the 4.29 and 3.65 eV emission bands of CsI:Pb can

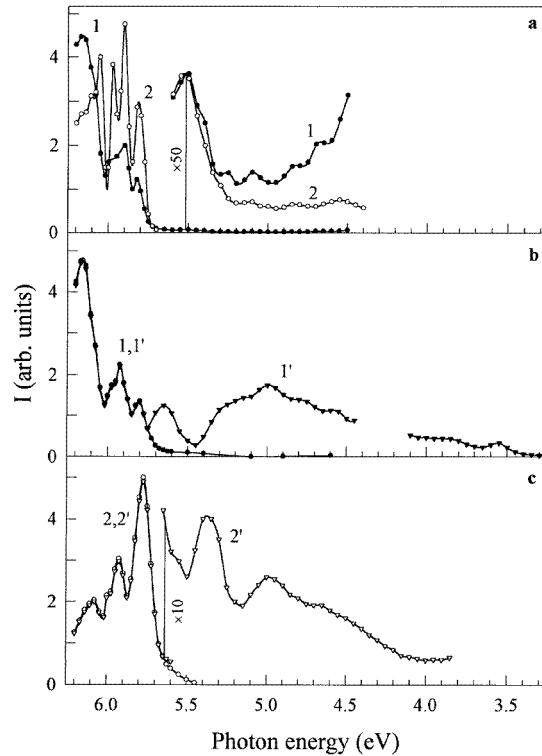


**Figure 2.** The dependences of the normalized intensities on the illumination time measured at 4.2 K for the 4.29 eV (curve 1) and the 3.65 eV (curve 2) emission of CsI:Pb under illumination (a) in the lead-induced 4.9 eV absorption band and (b) in the exciton 5.9 eV band.

be excited not only in the exciton bands but also in the optically created lead-induced absorption bands. It may be assumed that in the latter case this emission appears as a result of the  $\{e^- + V_K\}$  recombinations, i.e. the  $V_K$  and some electron lead centres are produced in the process of illumination.

### 3.3. Temperature dependences of the emission intensities

Under excitation in the exciton bands the temperature dependences of the intensity of the 4.29 and 3.65 eV emissions of CsI:Tl and CsI:Pb are very similar to those obtained in [8] and [11] for a pure CsI crystal (see figure 4(a)). Under excitation in the lead-induced absorption bands (after the illumination of the crystal at 4.2 K up to saturation) the  $I(T)$  dependences are also similar to those of pure CsI but only at the temperatures  $T < 10$  K (figure 4(b)): the intensity of the 4.29 eV band decreases sharply (curve 1) but the intensity of the 3.65 eV emission increases (curve 2). At 10–80 K a slow decrease of intensity is observed for the 3.65 eV emission, probably due to tunnelling processes. At  $T > 80$  K the intensity decreases more rapidly, and at 120 K the 3.65 eV emission is absent. The  $I(T)$  dependence in this temperature range is caused by the thermal destruction of the optically created centres, as after heating up to 120 K the characteristics of CsI:Pb at 4.2 K are the same as before the illumination. The thermal destruction of the optically created centres is accompanied by the appearance of the thermally stimulated  $\approx 2.95$  eV luminescence at 95 and 107 K (curve 3). This emission may appear as a result of the  $V_K$  recombinations with  $Na^0$  (see, e.g., [15]). However, unlike the case in [15], no TSL peaks are observed at  $T < 80$  K.



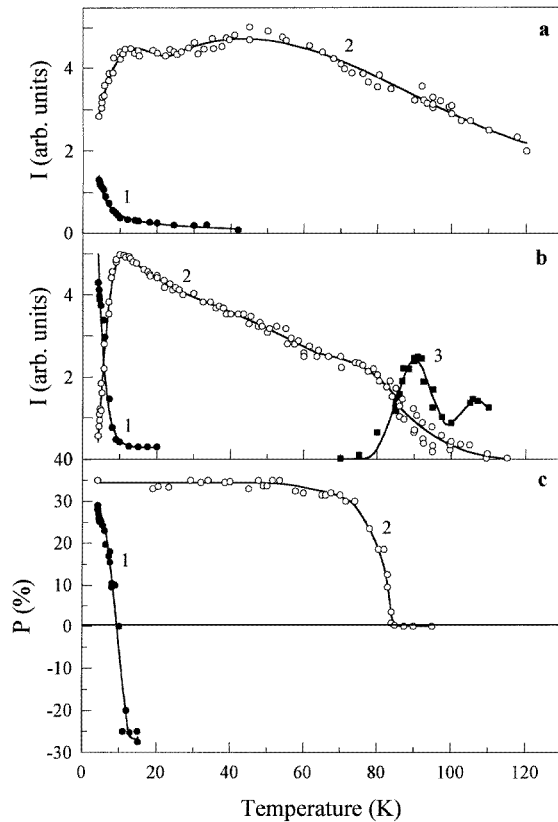
**Figure 3.** Excitation spectra of 4.29 eV (curves 1 and 1') and 3.65 eV (curves 2 and 2') emission measured at 4.2 K (a) for CsI:Ti and (b, c) for CsI:Pb crystals before (curves 1 and 2) and after (curves 1' and 2') the illumination of the crystal at 4.2 K until saturation.

### 3.4. Polarization of the 4.29 and 3.65 eV emission

After the illumination of CsI:Pb crystals in the lead-induced absorption bands (5.1–4.05 eV) until saturation no polarization of the 4.29 and 3.65 emission is observed. However, if after that the optically created  $V_K$  centres are aligned by unpolarized 410 nm light along the [100] direction, a strong  $\pi$  polarization of both the emission bands appears under excitation by photons of 5.8–3.4 eV energy and observation in the [010] direction perpendicular to the excitation light. The polarization degree  $P$  is about +34% for the 3.65 eV band and +28% for the 4.29 eV band and does not depend on the excitation energy.

The temperature dependences of the polarization degree (figure 4(c)) are very similar to those obtained in [8] for the  $\{e^- + V_K\}$  recombination luminescence in pure CsI. The polarization degree  $P$  of the 3.65 eV emission is constant up to about 55 K (curve 2). At temperatures near 80 K a sharp decrease of  $P$  is observed, which is caused by the reorientation of the  $V_K$  centres. At temperatures  $T > 4.2$  K the polarization degree of the 4.29 eV emission decreases sharply, changes sign near 10 K and reaches the value of  $-25\%$  at 13 K (curve 1). This means that at  $T > 10$  K the 4.29 eV emission is mainly  $\sigma$  polarized.

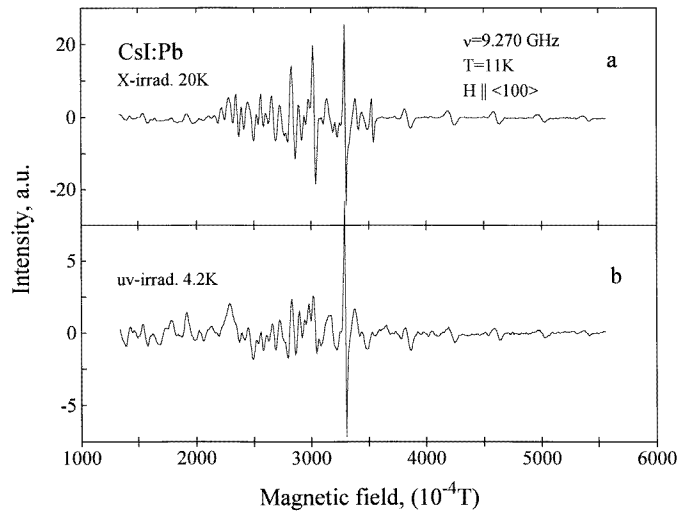
These results confirm our assumption that the 4.29 and 3.65 eV emission observed in CsI:Pb under 5.8–3.4 eV excitation really arises from the  $\{e^- + V_K\}$  recombinations.



**Figure 4.** Temperature dependences (a, b) of the intensities and (c) of the polarization degrees of the 4.29 eV (curve 1) and the 3.65 eV (curve 2) emission of CsI:Pb measured under excitation (a) in exciton bands and (b, c) in the optically created lead-induced absorption bands and the curve of the thermally stimulated luminescence with the maximum at 2.95 eV (curve 3).

### 3.5. ESR spectra

The illumination of CsI:Pb in the lead-induced absorption bands at 4.2 K gives rise to the ESR spectrum (figure 5(b)). After x-irradiation (50 kV, 15 mA) of the same crystal at  $\approx 20$  K we obtained a similar, but several times more intense spectrum (figure 5(a)). These ESR spectra could be compared with the ones given in [15] and [16] for x-irradiated CsI:Tl. It is evident that the spectra are essentially the same. The main lines belong to the  $V_K$  centres: the characteristic 11-line spectrum of the  $V_K$  centres parallel to the static magnetic field is clearly visible. On the low-field side the spectrum of the  $V_K$  centres is overlapped by the noiselike spectrum of the quartz sample tube. In addition to that, the three saturated orientation-independent lines belonging to the sample tube (the  $H^0$  centre doublet and a central line with  $g \approx 2.011$ ) are visible. At 11 K the ESR signal of the  $V_K$  centres did not saturate even at 20 mW microwave power. The number of  $V_K$  centres created by optical excitation was  $\sim 10^{14}$ . By illumination in the absorption band of the  $V_K$  centres at 3.02 eV alignment of the  $V_K$  centres was achieved.



**Figure 5.** ESR spectra of CsI:Pb after (a) x-irradiation (50 kV, 15 mA, 2 h) at 20 K and (b) UV irradiation ( $E = 4.4$  eV, 2 h) at 4.2 K.

#### 4. Discussion

A pure CsI crystal is well known to have two emission bands (4.3 and 3.7 eV) ascribed to the STE (see, e.g. [7–14] and references therein). The 4.3 eV emission belongs to the on-centre STE [11, 12]. The off-centre STE is responsible for the 3.7 eV emission [11–14]. According to [11], at 4.5 K the intensity of the 4.3 eV band under two-photon excitation by the 3.18 eV light is three times as large as that of the 3.7 eV band. As the temperature rises, a sharp redistribution of the intensities of the 4.3 and 3.7 eV emission bands occurs near 7–8 K, and at  $T > 10$  K the latter band becomes about 50 times as intense as the former one.

The comparison of these data with the results obtained in the present paper allows the conclusion that the characteristics of the STE emission in a pure CsI crystal and those of the 4.29 and 3.65 eV emission in CsI:Ti and CsI:Pb crystals are very similar. These emission bands are likely to be of the same origin. However, unlike the case in CsI:Ti, in CsI:Pb this emission is efficiently excited in the impurity-induced absorption bands in the 5.7–3.4 eV energy range. These bands of electronic nature as well as the  $V_K$  centres are optically created at 4.2 K, probably due to the photoionization of lead centres by the photons of 5.1–4.0 eV energy. The intense 4.29 and 3.65 eV emission bands appear as a result of the electron recombinations with the  $V_K$  centres. The optically created  $V_K$  centres become reoriented near 80 K and delocalized near 95 K. The mobile  $V_K$  centres recombine mainly with  $\text{Na}^0$ , giving rise to the 2.95 eV emission of the  $\text{Na}^+$ -perturbed STE. Some differences in the  $I(T)$  dependences of the 3.65 eV emission observed under excitation in the exciton and in the impurity absorption bands may be caused by tunnel recombinations of close defects.

Similar processes have been observed in [17], where the exciton emission of KI:In and KI:Sn crystals has been detected under excitation by high-power pulses of an XeCl laser (308 nm). These features have been explained as the photoionization of an impurity  $A^+$  ion:  $A^+ + h\nu \rightarrow A^{2+} + e^-$ , the subsequent delocalization of a hole from the  $A^{2+}$  ion:



$A^{2+} \rightarrow A^+ + V_K$ ), and the recombination of  $e^-$  and  $V_K$  centres.

As mentioned above, in CsI:Tl the 4.29 and 3.65 eV emission can be excited only within the exciton bands. However, the 2.55 and 2.25 eV emission bands of the  $Tl^+$ -perturbed off-centre exciton are excited mainly in the  $Tl^+$ -induced absorption bands. Under excitation in the 6.15–5.8 eV energy range their intensity is much smaller. It is interesting to note that, in spite of such a strong difference in the positions and characteristics of the above-mentioned exciton-like emission bands, the parameters of the RES responsible for the 3.65, 2.55 and 2.25 eV emission bands of CsI:Tl are very similar.

### Acknowledgments

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