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# Electronic structure of the orthorhombic and tetragonal phases of Tl<sub>3</sub>PbBr<sub>5</sub>

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## **Motivation of the study**

- The invention of a solid state laser cavity based on the low phonon energy crystal Pr<sup>3+</sup>:LaCl<sub>3</sub> at 5.2 and 7.2 µm by Bowman and co-workers [1] has stimulated a lot of attempts on development and investigation of non-linear optical crystals for middle infrared (mid-IR) and long-wavelength infrared (long-wave-IR) laser sources for their use as compact devices applied for remote sensing in bio-chemical agents, in the vibrational fingerprint region, free space communications, clinic and diagnostic analysis, ultra-sensitive detection of drugs and explosives, optical remote sensing technology LIDAR (Light Detection and Ranging), etc. These applications require high output power/energy and no moisture-sensitive high-purity materials at room-temperature operations. Nevertheless, LaCl<sub>3</sub> is strongly hygroscopic and, as a result, this material is difficult to handle as an efficient laser source operating in ambient conditions.
- As alternative host materials, in recent years, ternary lead halides have been identified as new low phonon energy hosts operating in mid-IR and long-wave-IR regions.

[1] S.R. Bowman, J. Ganem, B.J. Feldman, A.W. Kueney, IEEE J. Quantum Electron. 30 (1994) 2925–2928.

### **Motivation of the study**

- Those requirements have generated a great number of studies regarding elaboration of novel complex non-hygroscopic and non-linear optical low-phonon energy lead halides with the common formulas APb<sub>2</sub>X<sub>5</sub> and Tl<sub>3</sub>PbX<sub>5</sub> (where A = K, Rb; X = Cl, Br or I).
- The APb<sub>2</sub>X<sub>5</sub> and Tl<sub>3</sub>PbX<sub>5</sub> (A = K, Rb; X = Cl, Br, I) halides are capable to accept effective doping of rare-earth (RE) elements and mid-IR solid-state laser sources on RE iondoped lead halides pumped by conventional lasers (or diode-pumped solid state lasers) are found to be very promising for their application at ambient conditions.
- Among those lead bromides, trithallium lead pentabromide, Tl<sub>3</sub>PbBr<sub>5</sub>, is of particular interest.

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- The bromide possesses transparency ranging from 0.65 to at least 24 μm.
- Strong luminescence at around 4–5.5  $\mu$ m have been detected for  $Pr^{3+}:Tl_3PbBr_5$  single crystal and has been assigned to the  ${}^{3}H_5 \leftrightarrow {}^{3}H_4$  transition of the  $Pr^{3+}$  ions.
- Pr<sup>3+</sup>:Tl<sub>3</sub>PbBr<sub>5</sub> crystal was found to be very promising material for the development of a broadly tunable mid-IR solid-state laser source.
- Er<sup>3+</sup>:Tl<sub>3</sub>PbBr<sub>5</sub> was found to possess substantial emission cross sections in the band II of the atmosphere transparency window.
- Two polymorphous forms, namely orthorhombic low-temperature (LT) and tetragonal high-temperature (HT), have been detected for  $Tl_3PbBr_5$ , with a first-order phase transition occurring at 239 °C: the *LT*- $Tl_3PbBr_5$ phase crystallizes in the space group  $P2_12_12_1$ , with the lattice parameters a = 15.397 Å, b = 9.061 Å, and c = 8.537 Å, whilst the *HT*- $Tl_3PbBr_5$  phase possesses the lattice parameters a = b = 15.486 Å and c = 8.903 Å (space group  $P4_1$ ).

The packing of the polyhedra of the *LT*and *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> phases

> The packing of the polyhedra formed by bromine atoms surrounding lead atoms and the inter-atomic distances within the lead polyhedra in the structures of *LT*-Tl<sub>3</sub>PbBr<sub>5</sub> and *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> polymorphous forms





**Coordination polehedra of the** *LT***and** *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> **phases** 

> The coordination polyhedra of thallium atoms and the interatomic distances within these polyhedra in the structure of the both polymorpous forms of  $Tl_3PbBr_5$





Panoramic view of a piece of the as-grown Tl<sub>3</sub>PbBr<sub>5</sub> single crystal used in the present experimental studies

**Experimental and calculated X-ray diffraction patterns and their difference for** *LT***-Tl**<sub>3</sub>**PbBr**<sub>5</sub>

# Atomic positions for *LT*-Tl<sub>3</sub>PbBr<sub>5</sub> as determined by the XRD data

- Table
- Atomic positions for *LT*-TI<sub>3</sub>PbBr<sub>5</sub>

•	Atom	Wyckoff	Х	У	Z	$B_{iso} \times 10^2 \text{ (nm}^2\text{)}$
•		site				
•	Pb	4	0.0438(3)	0.2053(4)	0.8271(5)	1.18(11)
•	TI1	4	0.0379(3)	0.8407(4)	0.1895(5)	2.15(12)
	TI2	4	0.7289(3)	0.9210(4)	0.1626(5)	1.39(10)
•	TI3	4	0.8034(2)	0.4575(5)	0.0244(4)	1.29(12)
	Br1	4	0.2293(6)	0.2535(8)	0.6720(13)	1.1(3)
•	Br2	4	0.6436(6)	0.3050(11)	0.8525(12)	1.5(3)
•	Br3	4	0.6185(6)	0.6067(11)	0.1704(13)	0.9(3)
•	Br4	4	0.9752(6)	0.0432(11)	0.5209(11)	1.8(3)
•	Br5	4	0.4041(6)	0.4084(9)	0.9862(11)	2.1(3)

## **Methods of study**

#### **Theoretical:**

The first-principles band-structure full potential linearized augmented plane wave (FP-LAPW) method with the WIEN97 code was used for calculations of the total and partials DOS

Experimental: X-Ray photoelectron spectroscopy (XPS) [Mg Kα irradiation]

 Survey XPS spectra recorded for (1) pristine and (2) Ar<sup>+</sup> ion-bombarded surface of Tl<sub>3</sub>PbBr<sub>5</sub> single crystal.





• Detailed XPS (a) Tl 4d and Pb 4d and (b) Tl 4f and Pb 4f core-level spectra recorded for (1) pristine and (2) Ar+ ion-bombarded surface of the Tl<sub>3</sub>PbBr<sub>5</sub> single crystal



Detailed XPS (a) Br 3p and (b) Br 3d core-level spectra recorded for (1) pristine and
(2) Ar+ ion-bombarded surface of the Tl<sub>3</sub>PbBr<sub>5</sub> single crystal



XPS valence-band spectra (including upper Pb 5d and Tl 5d core-levels) recorded for (1) pristine and (2) Ar+ ionbombarded surface of the Tl<sub>3</sub>PbBr<sub>5</sub> single crystal



Plot of total DOS including upper core, valence-band (VB) and conduction-band (CB) states of the LT-Tl<sub>3</sub>PbBr<sub>5</sub> phase (*note*: the upper core states are labelled with respect to their dominant atomic contributions)



• (a) Total DOS, total and partial densities of states of (b) Tl, (c) Pb, and (d) Br atoms of the *LT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase

**Electronic bands along selected symmetry paths within the first Brillouin zone of the** *LT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase

- The dispersions of the curves near the valence-band maxima and conduction-band minima are rather flat in the *LT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase.
- The conduction band minimum is located at  $k=(0.0\ 0.5\ 0.475)$ , whilst the valence-band maximum is located at  $k=(0.0\ 0.5\ 0.350)$ .
- The LT-Tl<sub>3</sub>PbBr<sub>5</sub> phase is an indirectgap material with band gap of  $E_g = 3.05 \text{ eV}$ . This theoretical finding is in excellent agreement with the value  $E_g = 3.2 \text{ eV}$  derived experimentally for Tl<sub>3</sub>PbBr<sub>5</sub> crystal.









- XRD patterns recorded for Tl<sub>3</sub>PbBr<sub>5</sub> at room temperature (*LT*-Tl<sub>3</sub>PbBr<sub>5</sub>; bottom curve) and at 300 °C (*HT*-Tl<sub>3</sub>PbBr<sub>5</sub>; upper curve)
- Survey XPS spectrum recorded for the *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase at 300 °C





 Detailed XPS (a) Pb 4f, (b) Tl 4f, and (c) Br 3d core-level spectra recorded for the *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase at 300 °C



• (a) Total DOS, total and partial densities of states of (b) Tl, (c) Pb, and (d) Br atoms of the *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase





Plot of total DOS including upper core, valence-band and conductionband states of the HT-Tl<sub>3</sub>PbBr<sub>5</sub> phase (Note: Data of no spin-orbit coupling (NSOC) calculations). Plot of total DOS including upper core, valence-band and conductionband states of the *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase (Note: Data of spin-orbit coupling (SOC) calculations).



(a) Total DOS, total and partial densities of states of (b) Tl, (c) Pb, and (d) Br atoms of the *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase.(Note: Data of spin-orbit coupling (SOC) calculations).

#### **Electronic** bands along selected symmetry paths within the first **Brillouin zone of the HT-Tl<sub>3</sub>PbBr<sub>5</sub> phase**



- The dispersions of the curves near the valence-band maxima and conduction-band minima are
- rather flat in the HT-Tl<sub>3</sub>PbBr<sub>5</sub> phase. The conduction band minimum is located at the M point (0.5 0.5 0.0), whilst the valence-band maximum is located in the M– $\Gamma$  direction, namely at k=(0.304 0.304 0.0) The LT-Tl<sub>3</sub>PbBr<sub>5</sub> phase is an indirect-gap material with band gap of E<sub>g</sub> = 2.26 eV (NSOC) [E<sub>g</sub> =
- 1.76 eV (SŎC)].



• XPS valence-band spectrum (including upper Pb 5d and Tl 5d core-levels) recorded for the *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase at 300 °C (*Note*: XPS valence-band spectrum of the *LT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase is plotted in the inset, for comparison)

Results of FP-LAPW band-structure calculations of different *HT*-Tl<sub>3</sub>PbX<sub>5</sub> (X = Cl, Br) phases

Compound	Valence band width	Value of E <sub>g eV</sub>
<i>LT</i> -Tl <sub>3</sub> PbBr <sub>5</sub>	4.82 eV	3.05 eV [1]
<i>HT</i> -Tl <sub>3</sub> PbBr <sub>5</sub>	4.85 eV	2.26 eV [2]
HT-Tl <sub>3</sub> PbCl <sub>5</sub>	4.72 eV	2.73 eV [3]

- [1] O.Y. Khyzhun et al., Opt. Mater. 35 (2013) 1081-1089.
- [2] N.M. Denysyuk et al., J. Alloys Compd. 576 (2013) 271-278.
- [3] V.L. Bekenev et al., J. Phys. Chem. Solids 72 (2011) 705-713.

# **Electronic** bands along selected symmetry paths within the first **Brillouin** zone of the *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> phase



• Curves of broadening the total DOS of HT-Tl<sub>3</sub>PbBr<sub>5</sub> with the Lorenz parameters  $\gamma = 0.2$  to 1.0: (a) NSOC and (b) SOC calculations

# Conclusions

- Our XPS results indicate the low hygroscopicity and high chemical stability of Tl<sub>3</sub>PbBr<sub>5</sub> that is extremely important for handling this material as an efficient laser source operating in ambient conditions.
- The *ab initio* FP-LAPW calculations render that the dominant contributors in the valence-band region of the LT and HT polymorphous forms of Tl<sub>3</sub>PbBr<sub>5</sub> are the Br 4p-like states that contribute mainly into the top and the central portion of the valence band, while its bottom is composed mainly by contributions of the Tl 6s-like states.
- FP-LAPW data reveal that the bottom of the conduction band of *HT*-Tl<sub>3</sub>PbBr<sub>5</sub> is dominated by contributions of the Pb 6p\*-like states, in *LT*-Tl<sub>3</sub>PbBr<sub>5</sub> it is dominated by contributions of the Pb 6p\*- and Tl 6p\*- likes states in almost equal proportions.
- Our theoretical data indicate that the orthorhombic and tetragonal phases of  $Tl_3PbBr_5$ are indirect-gap materials with the band gap values of  $E_g = 3.05 \text{ eV} (LT-Tl_3PbBr_5)$  and  $E_g = 2.26 \text{ eV}$  and 1.76 eV for NSOC and SOC calculations of HT-Tl\_3PbBr<sub>5</sub>, respectively.
- Comparative measurements at 20 and 300 °C of XPS core-level spectra of the  $Tl_3PbBr_5$  single crystal indicate that the charge states of the atoms constituting the compound do not change during the orthorhombic (space group  $P2_12_12_1$ ) to tetragonal (space group  $P4_1$ ) transition.
- We have detected some shift (about 0.3 eV) of the XPS valence-band spectrum towards the Fermi level when going from LT-Tl<sub>3</sub>PbBr<sub>5</sub> to HT-Tl<sub>3</sub>PbBr<sub>5</sub>. This valence-band shift is found to be in agreement with our theoretical FP-LAPW predictions of decreasing the band gap value when the crystal structure of Tl<sub>3</sub>PbBr<sub>5</sub> changes from the orthorhombic  $(P2_12_12_1)$  to tetragonal  $(P4_1)$ .

# Thank you for your attention!