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# Crystal growth and the electronic structure of $Tl_3PbCl_5$

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ABSTRACT

Total and partial densities of states of constituent atoms of two tetragonal phases of $Tl_3PbCl_5$ (space groups $P4_12_12$ and $P4_1$) have been calculated using the full potential linearized augmented plane wave (FP-LAPW) method and Korringa–Kohn–Rostoker method within coherent potential approximation (KKR-CPA). The results obtained reveal the similarity of occupations of the valence band and the conduction band in the both tetragonal phases of $Tl_3PbCl_5$. The FP-LAPW and KKR-CPA data indicate that the valence band of $Tl_3PbCl_5$ is dominated by contributions of the Cl 3p-like states, which contribute mainly to the top and the central portion of the valence band with also significant contributions throughout the whole valence-band region. Further, the bottom of the valence band of $Tl_3PbCl_5$ is composed mainly of the Tl 6s-like states, while the bottom of the conduction band is dominated by contributions of the empty Pb 6p-like states. The KKR-CPA results allow to assume that the width of the valence band increases somewhat while band gap, $E_g$, decreases when changing the crystal structure from $P4_12_12$ to $P4_1$. The X-ray photoelectron core-level and valence-band spectra for pristine and $Ar^+$-ion-irradiated surfaces of a $Tl_3PbCl_5$ monocrystal grown by the Bridgman–Stockbarger method have been measured.

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## 1. Introduction

In recent years a lot of attention has been paid to technologies of development and investigation of non-linear optical crystals for middle infrared (3–12 μm) laser sources for applications in free space communications, remote sensing, medical diagnostics, etc. [1]. Such applications require high output power/energy, stable and compact devices as well as no moisture-sensitive materials at room-temperature operations [1]. In the past, chalcogenides and rare-earth chlorides, partly $Dy^{3+}$:$CaGa_2S_4$ lasing at 2.43 and 4.31 μm [2] and $Pr^{3+}$:$LaCl_3$ lasing at 5.2 and 7.2 μm [3,4], were considered as promising laser crystalline hosts for middle infrared (mid-IR) applications. Nevertheless, these crystals are found to be strongly hygroscopic; this disadvantage prevents their development as efficient laser sources. The requirement of non-hygroscopic materials has generated a number of investigations regarding growth of several no moisture-sensitive complex halide-bearing crystals to find alternative solutions. Among promising halides for mid-IR laser applications, $KPb_2Cl_5$, $KPb_2Br_5$, $RbPb_2Br_5$, $CsCdBr_3$, $Tl_4HgI_6$, $Tl_4PbI_6$, $Tl_3PbBr_5$, $Tl_3PbI_5$, $Tl_3PbCl_5$, etc. have been reported [1,4–11]. $Tl_3PbCl_5$ halide is of particular interest. $Tl_3PbCl_5$ crystallizes [12] in the $TlCl–PbCl_2$ system, which melts congruently at 395 °C [5]. $Tl_3PbCl_5$ single crystals are transparent in the range of 0.5–20 μm, non-hygroscopic and uniaxial [11]. An elliptically deformed circular cross-section is characteristic of $Tl_3PbCl_5$ single crystals that can be easily grown from the liquid state by the Bridgman–Stockbarger method [11].

Two phases, both possessing a tetragonal symmetry (Fig. 1), have been reported for $Tl_3PbCl_5$. Keller [13] was first to solve a crystalline symmetry and to determine unit cell parameters of $Tl_3PbCl_5$ on single crystals grown from liquid state; however, his space group for this compound ($P4_1$) was not confirmed by other authors. Partly, Skarstad et al. [14] have reported that grown by the Bridgman method $Tl_3PbCl_5$ single crystals crystallize in a tetragonal symmetry with four formula units per unit cell, but in the non-centrosymmetric space group $P4_12_12$ (no. 92). Owing to this space group, both $Tl^+$ and $Pb^{2+}$ cations occupy the equivalent 8b sites (Table 1). Therefore, the formula for this compound can be appropriately written as $(Tl_{0.75}Pb_{0.25})_4Cl_5$ [14]. The findings by Skarstad et al. [14] have been confirmed comparatively recently by detailed X-ray single-crystal diffraction

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measurements [11] on $Tl_3PbCl_5$ grown by the Bridgman–Stockbarger method (see Table 1).

In 1983, based on differential thermal analysis, Keller [5] reported for $Tl_3PbCl_5$ the existence of a first-order phase transition occurring at 155 °C. The above first-order transition was suggested to be due to the ordering of $Tl^+$ and $Pb^{2+}$ cations leaving unchanged positions of $Cl^-$ anions [5]. Lattice parameters and atomic positions of this ordered $Tl_3PbCl_5$ phase crystallizing in a tetragonal symmetry with four formula units per unit cell (space group $P4_1$; no. 76) are listed in Table 2. Ferrier et al. [11] confirmed a phase transition in $Tl_3PbCl_5$, however occurring at 171 °C (instead of 155 °C reported by Keller [5]). Nevertheless, Ferrier et al. [11] were unable to interpret this transition occurring in $Tl_3PbCl_5$.

To the best of our knowledge, the electronic structure of $Tl_3PbCl_5$ was not studied both from a theoretical and an experimental point of view. Therefore, in the present paper we aim at a comprehensive study of the energy distribution of electronic states of different symmetries of constituent atoms of $Tl_3PbCl_5$. With this purpose, we employ possibilities of the full potential linearized augmented plane wave (FP-LAPW) method as incorporated in the WIEN97 code [15] in order to study total density of states (DOS) and partial densities of states of the ordered $Tl_3PbCl_5$ phase crystallizing in the space group $P4_1$ (no. 76). For clarity, we shall refer to this phase as high-temperature (HT) $Tl_3PbCl_5$. Additionally, the electronic structure of the $Tl_3PbCl_5$ phase with statistical occupation of the equivalent 8b sites by $Tl^+$ and $Pb^{2+}$ cations (space group $P4_12_12$; no. 92; we shall refer to this phase as room-temperature (RT) $Tl_3PbCl_5$) was calculated employing the possibility of the Korringa–Kohn–Rostoker method within coherent potential approximation (KKR-CPA) [16]. The latter method was used also to calculate the electronic structure of the HT-$Tl_3PbCl_5$ phase. Further, we have used possibilities of the X-ray photoelectron spectroscopy (XPS) method to study the XPS valence-band spectrum as well as to measure the binding energies (BEs) of core-level electrons of constituent atoms of RT-$Tl_3PbCl_5$. The influence of 1.5 keV $Ar^+$ bombardment on the XPS valence-band and core-level spectra of RT-$Tl_3PbCl_5$ surface is also within the scope of the present study. For experimental measurements, we have used a $Tl_3PbCl_5$ crystal grown by the Bridgman–Stockbarger method.

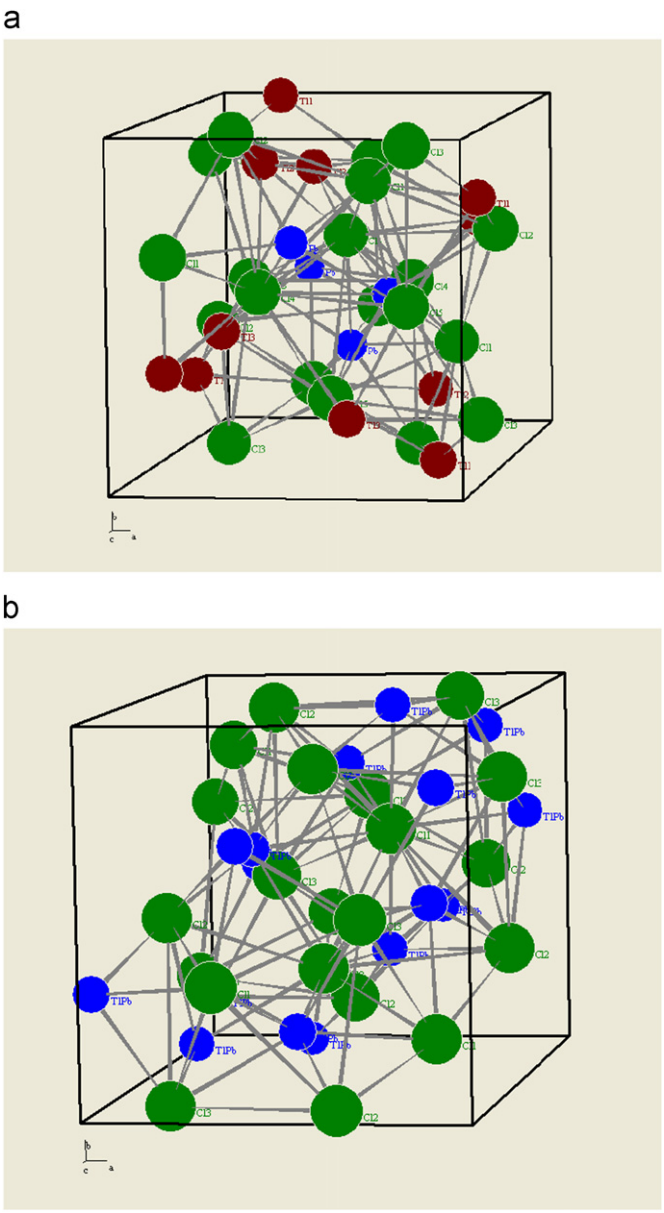


**Fig. 1.** Crystal structure of (a) HT-$Tl_3PbCl_5$ (space group $P4_1$; no. 76; Cl—large green balls, Tl—middle brown balls and Pb—small blue balls) and (b) RT-$Tl_3PbCl_5$ (space group $P4_12_12$; no. 92; Cl—large green balls, Tl and Pb—small blue balls) phases. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 2**
Crystallography data for atomic coordinates of the HT-$Tl_3PbCl_5$ phase (space group $P4_1$; no. 76) as determined by Keller [13].

| Atom | Wyckoff position | $a$=8.448 Å and $c$=14.912 Å (ICSD #1262) | | |
|---|---|---|---|---|
| | | $x$ | $y$ | $z$ |
| Tl1 | 4a | 0.9942 | 0.8074 | 0.8030 |
| Tl2 | 4a | 0.1212 | 0.3198 | 0.8786 |
| Tl3 | 4a | 0.6216 | 0.1804 | 0.8211 |
| Pb | 4a | 0.4940 | 0.6936 | 0.8963 |
| Cl1 | 4a | 0.3370 | 0.1570 | 0.2310 |
| Cl2 | 4a | 0.6870 | 0.0080 | 0.3540 |
| Cl3 | 4a | 0.0260 | 0.8390 | 0.2100 |
| Cl4 | 4a | 0.5280 | 0.6500 | 0.5080 |
| Cl5 | 4a | 0.4900 | 0.8060 | 0.1080 |

**Table 1**
Crystallography data for atomic coordinates of the RT-$Tl_3PbCl_5$ phase (space group $P4_12_12$; no. 92) as determined in Refs. [11,14].

| Atom | Wyckoff position | $a$=8.450 Å and $c$=14.927 Å (Ref. [14]) (ICSD #8151) | | | $a$=8.44 Å and $c$=14.92 Å (Ref. [11]) | | |
|---|---|---|---|---|---|---|---|
| | | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| Tl/Pb1 | 8b | 0.3067 | 0.0066 | 0.07832 | 0.30665 | −0.00683 | 0.671618 |
| Tl/Pb2 | 8b | 0.8193 | 0.8787 | 0.1538 | 0.68069 | −0.37899 | 0.65376 |
| Cl1 | 4a | 0.3420 | 0.3420 | 0.0000 | 0.1601 | 0.1601 | 0.5 |
| Cl2 | 8b | 0.3480 | 0.9740 | 0.4755 | 0.0132 | −0.1880 | 0.62292 |
| Cl3 | 8b | 0.1880 | 0.0120 | 0.874 | 0.4741 | −0.15220 | 0.52469 |

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