X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF THE ELECTRONIC STRUCTURE OF Tl_3PBBR_5 AND $TLPB_2BR_5$ SINGLE CRYSTALS

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Thallium dilead pentabromide, $TlPb_2Br_5$, and trithallium lead pentabromide, Tl_3PbBr_5, stand among bromides as promising host materials, in particular for their application to eye-safe solid-state lasers and optical communications. The existence of Tl_3PbBr_5 and $TlPb_2Br_5$ compounds was first detected when studying the pseudo-binary TlBr-$PbBr_2$ system. The $TlPb_2Br_5$ compound crystallizes in the monoclinic structure, space group $P2_1/c$, with the lattice parameters a=9.304(4)Å, b=8.336(3)Å, and c=13.004(5)Å, while Tl_3PbBr_5 is orthorhombic (the space group $P2_12_12_1$, with the lattice parameters a = 15.397 Å, b = 9.061 Å, and c = 8.537 Å).

In the present work, Tl_3PbBr_5 and $TlPb_2Br_5$ single crystals have been successfully grown by the Bridgman-Stockbarger method. As an example, Fig. 1 presents a photo image of a piece of the as-grown $TlPb_2Br_5$ single crystal.

Fig. 1 Photo of a piece of the $TlPb_2Br_5$ single crystal used in the present experimental studies

Survey XPS spectra of pristine and Ar^+-ion irradiated surfaces of the $TlPb_2Br_5$ single crystal are presented in Fig. 2. It is obvious that all the spectral features, except the C and O 1s levels and Auger KLL spectra for pristine surface, are attributed to the constituent element core-levels and Auger lines.

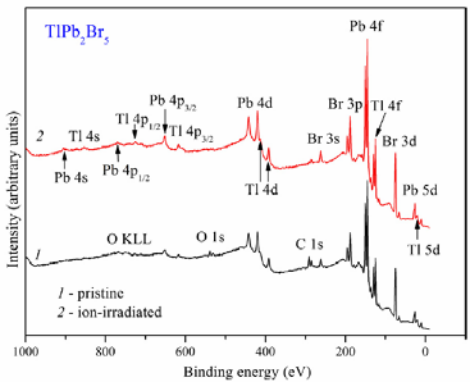

Fig. 2 Survey XPS spectra recorded for (1) pristine and (2) Ar^+ ion-bombarded surface of the $TlPb_2Br_5$ single crystal

Furthermore, as can be seen from Fig. 2, the present survey XPS data indicate that there is no active chemical interaction with oxygen when the $TlPb_2Br_5$ single crystal surface contact with air for a comparatively long time (several weeks). The survey XPS spectra presented in Fig. 2 display that the O 1s line is rather weak on the pristine surface studied and no trace of the O 1s signal is detected after the Ar^+ ion-bombardment of the surface of the $TlPb_2Br_5$ single crystal. Our results indicate the low hygroscopicity of $TlPb_2Br_5$, the property that is very important for handling this material as an efficient laser source operating in ambient conditions.

We have also made ab initio band-structure calculations of Tl_3PbBr_5 and $TlPb_2Br_5$ adopting the full potential linearized augmented plane wave method. The calculations reveal that the Tl_3PbBr_5 and $TlPb_2Br_5$ compounds are indirect-gap materials with band gaps of 3.05 and 2.92 eV, respectively.