Preparation, Crystal Structure, Properties, and Electronic Band Structure of $TlTaSe_3$

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Z. Naturforsch. **60b,** 858 – 866 (2005); received June 10, 2005

$TlTaSe_3$ was prepared from a fused mixture of $Tl_4Ta_2Se_{11}$, Ta and Se in the molar ratio 1:2:1. The compound shows dimorphism with H-$TlTaSe_3$, hexagonal, space group $P6_3/mmc$, $a = 7.2436(6)$, $c = 5.9736(6)$ Å, $c/a = 1.213$ and O-$TlTaSe_3$, orthorhombic, space group $Pnma$, $a = 9.554(13)$, $b = 3.6244(6)$, $c = 14.7271(17)$ Å. The crystal structure of H-$TlTaSe_3$ is isotypic to $BaVSe_3$ whereas that of O-$TlTaSe_3$ is closely related to the NH_4CdCl_3-type. Characteristic features of the structures are: $^1_\infty[TaSe_3{}^{2-}]$ chains of regular octahedra sharing faces along [001] for the hexagonal form and columns of double edge-sharing octahedra $^1_\infty[Ta_2Se_6{}^{2-}]$ running along [010] for O-$TlTaSe_3$. The columns are each separated by Tl^+ ions with the coordination number CN = 12 and CN = 8 respectively. The structures are compared and discussed in context with other isotypic structures of chalcogenides. The orthorhombic modification O-$TlTaSe_3$ is a semiconductor while H-$TlTaSe_3$ shows conventional metallic behaviour. The electronic structures of both modifications are discussed on the base of band structure calculations performed within the framework of density functional theory.

Key words: Thallium Tantalum Selenide, Crystal Structure, Dimorphic, Properties, Electronic Band Structure