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# Darstellung und Strukturaufklärung von Chalkogenid-Halogeniden des Bismuts

## Abstract


Within the three phase systems **$Bi_2O_3$–$BiX_3$ (X = Cl, Br, I),** single crystals of $Bi_4O_5Cl_2$, $Bi_{24}O_{31}X_{10}$ (X = Cl, Br), and $Bi_7O_9I_3$ were grown by chemical vapour transport. Single crystals of $Bi_5O_7I$ and $Bi_5O_7Br$ were grown at ambient temperature by addition of diluted $H[BiX_4]$ solutions to 5 N KOH. The crystal structure of $\alpha$-$Bi_5O_7I$ has been redetermined and refined to $R_1$ = 0.0375. It is completely different from the structures of $\beta$-$Bi_5O_7I$ and $Sb_5O_7I$ but shows a close relationship to the structure of BiOI. Structure analysis of $Bi_3O_4Cl$ revealed that the structure consists of alternating layers of $[Bi_3O_4]^+$ and $Cl^-$; they are arranged in the same way as in the structure of $Bi_3O_4Br$. The crystal structures of $Bi_{24}O_{31}X_{10}$ have been redetermined. The obtained structure models confirm a large part of literature model, but differ from it in some details of the O substructure. For $Bi_{24}O_{31}Cl_{10}$, a twofold superstructure of the literature model was found in addition.

In the system **$Bi_2Se_3$–$BiCl_3$,** single crystals of a compound which was previously known as "$Bi_8Se_9Cl_6$" (60 mole-% $Bi_2Se_3$) were obtained by chemical vapour transport (CVT). The crystal structure has been determined and refined to $R_1$ = 0.041. It is similar to the known structure of $Bi_{11}Se_{12}Cl_9$ but differs from it by a weak fourfold superstructure. The model is partially disordered and is closely related to the structure of BiSeCl. With respect to the (Bi,Se) substructure it consists of "folded ladders" parallel to the **b**-axis. The chemical formula is mostly consistent with $Bi_{11}Se_{12}Cl_9$ (57.1 mole-% $Bi_2Se_3$).

Within the system **$Bi_2Se_3$–$BiBr_3$,** single crystals of $Bi_3Se_4Br$ were grown by CVT. The crystal structure has been refined to $R_1$ = 0.0367. With respect to its (Bi,Se) substructure it is related to orthorhombic $Bi_2Se_3$ and to $Bi_{19}S_{27}Br_3$.

The new quaternary compounds **$ABi_6O_9X$ (A/X = Na/Br, Na/I, K/Cl, K/Br, K/I, Rb/Br, Rb/I)** were synthesized at ambient temperature by reaction of $BiX_3$ or $H[BiX_4]$ solution with > 10 N KOH or solid KOH. Single crystals of $KBi_6O_9X$ (X = Cl, Br, I) and of $NaBi_6O_9Br$ were grown by addition of diluted $H[BiX_4]$ solutions to > 10 N KOH. The crystal structures were solved by single crystal structure analysis and refined to $R_1$ = 0.0214, 0.0199, 0.0205, and 0.0150 respectively. In addition to that, Rietveld refinements for all seven compounds were performed. All $ABi_6O_9X$ compounds are isotypic; they crystallize in a new structure type with space group $Ia\bar{3}d$. The A, Bi, X positions correspond to a distorted *bcc* lattice. The (A,X) substructure consists of arrays of nonintersecting linear "chains" parallel to ⟨1 1 1⟩.