2D antimony oxide in K$_2$(Sb$_2$O$_3$)$_2$Te and an unusual optoelectronic behaviour

Huanyu He$^1$, Ralf Albrecht$^1$, Kati Finzel$^1$, Michael Rüsing$^1$, Michael Ruck$^{1,2}$

$^1$Technische Universität Dresden, Dresden, Germany $^2$Max-Planck Institute for Chemical Physics of Solids, Dresden, Germany

huanyu.he@tu-dresden.de

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We are currently investigating the potential of the novel synthesis approach 'hydroflux', which is intermediate between the alkaline salt flux and the hydrothermal synthesis method as proposed by zur Loye et al. in 2013.$^{[1]}$ This method utilizes approximately an equimolar ratio of hydroxide (e.g. KOH) to water, corresponding to concentrations such as 50 M KOH. The high number of new compounds discovered with this method suggest that hydroflux is a unique reaction medium.$^{[2]}$ Acid-base as well as redox chemistry are substantially different from established approaches. This is directly connected to the strong hydrophilicity of the hydroflux. In addition, the use of rather inexpensive Teflon-lined autoclaves, relatively low temperatures (150-250 °C) and short reaction times (within a few hours) make this synthetic method extremely promising. Moreover, crystals with sizes up to centimeters have been grown from hydroflux.

Using this approach, shiny green, air-stable single-crystals of the layered oxide telluride K$_2$(Sb$_2$O$_3$)$_2$Te (Fig.1a, 1b) were synthesized starting from TeO$_2$ and Sb$_2$O$_3$ in a potassium hydroxide hydroflux. The reduction of tellurium(IV) to tellurium( II) in the hydroflux has recently been investigated in detail in our group.$^{[3]}$ The synthesis of K$_2$(Sb$_2$O$_3$)$_2$Te was achieved through the addition of excess Sb$_2$O$_3$ as reducing agent that is oxidized to antimonate(V). Single-crystal X-ray diffraction revealed a rhombohedral layered structure (space group $R\overline{3}m$) with lattice parameters $a = 569.31(3)$ pm and $c = 2744.55(13)$ pm at 100(1) K (Figure.1c, 1d). The unprecedented honeycomb Sb$_2$O$_3$ layer (not known as a polymorph) is uncharged but polar with all antimony cations residing on one side. However, both orientations of the ferroelectric layer exist, connected by inversion symmetry. Potassium cations reside in the gap between two adjacent Sb$_2$O$_3$ layers that face each other with their oxide sides, telluride anions between the layer faces formed by antimony atoms.

The green metallic luster of K$_2$(Sb$_2$O$_3$)$_2$Te is highly unusual. The investigation of the optical and electronic properties in combination with electronic band structure calculations revealed a plethora of exceptional properties, such as compound-intrinsic transistor and varistor behavior, energy up-conversion in steps of 1.3 eV and 2.5 eV, enhancement of electrical conductivity by light of low energy (700 nm), but insulating behavior under light of high energy (300 nm).

Figure 1. (a): Crystals obtained from hydroflux; (b) scanning electron microscopy (SEM) image of the crystal; (c): Crystal structure of K$_2$(Sb$_2$O$_3$)$_2$Te. (d): Top view of a Sb$_2$O$_3$ honeycomb layer and the K···Te···K “dumbbells” that penetrate the layer perpendicularly.