From Yellow to Black: New Semiconducting Ba Chalcogeno-Germanates

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Dedicated to Professor Kurt O. Klepp on the occasion of his 60th birthday

The new germanates $Ba_2GeSe_{4-\delta}Te_\delta$ ($\delta < 2.5$) were prepared by reacting the elements under exclusion of air at 800 °C, followed by slow cooling to room temperature. These germanates form the Sr_2GeS_4 type, monoclinic space group $P2_1/m$, with lattice dimensions of $a = 699.58(4)$, $b = 709.38(4)$, $c = 917.38(6)$ pm, $\beta = 109.135(1)°$, $V = 430.11(4) \cdot 10^6$ pm^3 ($Z = 2$) for Ba_2GeSe_4. The structure contains isolated $GeSe_4$ tetrahedra. The oxidation states are assigned to be Ba^{II}, Ge^{IV}, and Se^{-II}. The yellow color of this ortho-seleno-germanate is indicative of semiconducting behavior with an activation energy of 2.6 – 3.0 eV, and the black appearance of the seleno-telluro-germanates points towards gaps < 1.7 eV. Electronic structure calculations based on the LMTO approximation resulted in smaller gaps of 1.7 – 0.8 eV, a tendency that is typical for this calculation method.

Key words: Electronic Structure, Semiconductor, Germanium, Selenium, Tellurium