Physico-Chemical nanomaterials science
On combine-layered nanoclustering in As-enriched sulfides

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Ab initio quantum-chemical modeling within CINCA (cation-interlinking network cluster approach) algorithm is employed to examine structure-forming tendencies in As-enriched binary As-S compounds. The As_4S_n nanoclusters with n=0,1,2,3,4 corresponding to average coordination numbers Z=3.00-2.50 (i.e. the number of bonds per atom of structure-forming unit) are selected to reflect expected network-, molecular- and combine-layered trends. Following fundamental finding of Bonazzi et al. [1] on origin of mineral duranusite As_4S possessing an orthorhombic structure composed of two layers (As_2 and As_2S), the formation energies are extrapolated for As_4S_2, As_4S_3 and As_4S_4 nanoclusters. In respect to the calculations performed, *the molecular-forming tendency* is shown to be better for As_4S_3 and As_4S_4 compositions (with respective mineral dimorphite and realgar), while As_4S_2, As_4S and As_4 compounds were dominated with an obvious *combine-layered tendency* resulting in energetically-favorable structure represented by mineral duranusite As_4S and orthorhombic As [2]. This result contradicts entirely to Kyono [3], who hypothesized molecular structure for duranusite As_4S.

From this viewpoint, it is predicted the existence of orthorhombic counterpart of As_4S_2 sulfide with Z=2.67, the traces of these orthorhombic crystallites being probably expected among known arsenic sulfides minerals.

1. *Bonazzi P., Lepore O., Bindi L.,* Molecular *versus* layered structure in arsenic sulphide minerals: the case of duranusite, As_4S // Eur J Mineral.-**28.**-P. 147-151.
2. *Smith P.M., Leadbetter A.J., Apling A.J.* The structure of orthorhombic and vitreous arsenic // Phil Mag.-1975.-**31**.-P. 57-64.
3. *Kyono A.,* Ab initio quantum chemical investigation of arsenic sulfide molecular diversity from As_4S_6 and As_4 // Phys Chem Mineral.-2013.-**40**.-P.717-731.