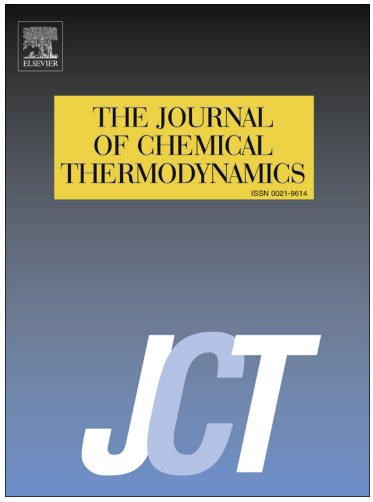

Thermal-alteration interphase transformations in natural and synthetic arsenic sulfide polymorphs

Oleh Shpotyuk, Andrzej Kozdras, Peter Balá ž, Zdenka Bujň áková, Yaroslav Shpotyuk

PII: S0021-9614(18)30253-2
DOI: https://doi.org/10.1016/j.jct.2018.08.019
Reference: YJCHT 5507

To appear in: *J. Chem. Thermodynamics*

Received Date: 29 March 2018
Revised Date: 10 August 2018
Accepted Date: 12 August 2018

Please cite this article as: O. Shpotyuk, A. Kozdras, P. Balá ž, Z. Bujň áková, Y. Shpotyuk, Thermal-alteration interphase transformations in natural and synthetic arsenic sulfide polymorphs, *J. Chem. Thermodynamics* (2018), doi: https://doi.org/10.1016/j.jct.2018.08.019

Thermal-alteration interphase transformations in natural and synthetic arsenic sulfide polymorphs

Oleh Shpotyuk[1,2*], Andrzej Kozdras[3], Peter Baláž[4], Zdenka Bujňáková[4], Yaroslav Shpotyuk[5,6]

[1] Jan Dlugosz University in Czestochowa
13/15, al. Armii Krajowej, 42201, Czestochowa, Poland
[2] Vlokh Institute of Physical Optics
23, Dragomanov str., 79005, Lviv, Ukraine
[3] Opole University of Technology
75, Ozimska str., 45370, Opole, Poland
[4] Institute of Geotechnics of the Slovak Academy of Sciences
45, Watsonova str., 04001, Košice, Slovakia
[5] Ivan Franko National University of Lviv
107, Tarnavskogo str., 79017, Lviv, Ukraine
[6] Centre for Innovation and Transfer of Natural Sciences and Engineering Knowledge, University of Rzeszow, 1, Pigonia str., 35-959, Rzeszow, Poland

*Corresponding author: olehshpotyuk@yahoo.com

Abstract

Thermal-alteration interphase transformations in natural (realgar α-As_4S_4 of two mineral origins) and synthetic (commercial powdered high-temperature β-As_4S_4 modification synthesized from elemental constituents and subjected to high-energy mechanical ball milling) arsenic monosulfide polymorphs are studied exploring temperature-modulated DSC TOPEM® method.

Specific heat capacity and non-reversing heat flow variations in realgar α-As_4S_4 demonstrate two endothermic events, these being ascribed to interphase α→β transformation at ~(540-550) K, and melting of this newly-formed high-temperature β-As_4S_4 phase at 581-582 K. This polymorph originated from thermal alteration of mineral realgar possesses congruent melting in contrast to synthetic β-As_4S_4 polymorph, which shows non-equilibrium melting due to accompanied generation of compositionally-authentic amorphous phase. Calorimetric studies on synthetic β-As_4S_4 in powdered coarse-grained and milled states demonstrate complicated non-equilibrium melting in principally different crystalline-amorphous environments along with crystal-to-glass transformation. Structural-chemical heterogeneity of β-As_4S_4 crystallites results in incongruent double-peak melting through two endothermic events at ~578 K and ~588 K. The amorphous phase formed under high-energy milling of synthetic β-As_4S_4 possesses a dual nature due to stabilization of As-rich glassy substances with low- and high-temperature glass transition mid-points. This process in the powdered synthetic β-As_4S_4, identified as re-amorphization of initial amorphous phase and direct vitrification from β-As_4S_4 crystallites, was parameterized as compared to calorimetric thermal-alteration events in orpiment As_2S_3 mineral.

Keywords: thermal alteration; interphase transformation; specific heat capacity; amorphization; mechanical milling; realgar α-As_4S_4