"Physico-Chemical nanomaterials science"

Free volume study of mechanochemically-amorphized nanoarsenicals with PAL spectroscopy

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The crystal-to-amorphous transition is probed by positron annihilation lifetime (PAL) spectroscopy exploring conventional fast-fast coincidence ORTEC system of high resolution using a set of arsenicals (arsenic sulfide As-S compounds):
(i) crystalline polymorphs of defined chemical compositions, i.e. As_2S_3 (mineral orpiment from WanShanChang Mine, Tongren, Guizhou Province, China) and α-As_4S_4 (mineral realgar from Realgar Mine, Hunan Province, China);
(ii) bulk glassy plates cut from melt-quenched As_xS_{100-x} ingots (x=30-42);
(iii) amorphous-crystalline pellets prepared from mechanochemically-milled (in a dry mode) As_xS_{100-x} alloys (glassy x=40; crystalline-amorphous x=45, 50; and polycrystalline x=56-66) and multiparticle nanocomposites (As_4S_4-ZnS/Fe_3O_4).

The experimental PAL spectra were reconstructed under decomposition into three single exponentials (with normalized component intensities), covering channels caused by positrons annihilating in defect-free bulk, trapped in spatially-extended free-volume defects and forming bound positron-electron (positronium Ps) states. The formalism of Ps-to-positron trapping conversion (x3-x2-coupling decomposition algorithm) was applied to parameterize free-volume evolution in nanostructurized millled nanoarsenicals.

Because of preferentially the same type of covalent bonding contributing to free volumes due to bond-free solid angles, close similarity between positron trapping centers is identified in realgar and other arsenicals (in part, in As-S glasses including stoichiometric As_2S_3). With these results we conclude that ratio of average positron lifetime can really serve as a criterion of crystal-to-glass transition in nanoarsenicals, provided these boundary states (crystalline and amorphous) are represented adequately, i.e. without additional positron- and Ps-trapping sites originated from any technological peculiarities.