Low temperature structural investigations along the Cu_3SbS_3 (skinnerite) - Cu_3BiS_3 (wittichenite) join.

Neil E. Johnson, Department of Geosciences, Virginia Tech, Blacksburg, VA
Elinor C. Spencer, Department of Geosciences, Virginia Tech, Blacksburg, VA
Nancy L. Ross, Department of Geosciences, Virginia Tech, Blacksburg, VA

The majority of minerals in the Cu-Sb-Bi-S system occur in the pseudoternary section defined by Cu_2S (chalcocite), Sb_2S_3(stibnite) and Bi_2S_3 (bismuthinite). Within this section, stibnite and bismuthinite and $CuSbS_2$ (chalcostibite) and $CuBiS_2$ (emplectite) are isostructural pairs displaying complete solid solution along their respective joins. In contrast, Cu_3SbS_3 (skinnerite) and Cu_3BiS_3 (wittichenite) are not isostructural at ambient temperature and a miscibility gap from 10 to 50 atomic percent bismuth has previously been described at 648K. Prior crystallographic investigation of these end-member phases has indicated significant polymorphism, mostly at elevated temperatures.

End-member Cu_3SbS_3 and Cu_3BiS_3 along with intermediate compositions with Sb:Bi ratios of 75:25, 50:50 and 25:75 were synthesized in evacuated silica glass tubes at temperatures between 675 and 693K and their structures determined and refined at temperatures ranging from 293 to 100K. Pure Cu_3SbS_3 is $P2_1/c$ at 293K but converts to a $P2_12_12_1$ form isostructural with pure Cu_3BiS_3 below approximately 250K, as previously reported. Compositions at Sb:Bi ratios of 75:25 and 50:50 adopt the $P2_12_12_1$ Cu_3BiS_3 structure over the entire temperature range examined. Pure Cu_3BiS_3 converts to a previously unknown phase of space group $Pnm2_1$ below approximately 250K and the composition at an Sb:Bi ratio of 25:75 adopts this structure below approximately 175K.

Equipment limitations prevented studies above 293K or below 100K, however we infer that a change from $P2_12_12_1$ to $Pnm2_1$ may occur around 50K for the 50:50 composition and that changes from $P2_12_12_1$ to $P2_1/c$ may occur for the 75:25 and 50:50 compositions at temperatures between 293 and 400K. Given the increasing interests in copper bearing sulfosalt minerals as energy technology materials, further investigations at wider temperature ranges are warranted.