Preparation and Crystal Structures of Ternary Rare Earth Silver and Gold Arsenides $LnAgAs_2$ and $LnAuAs_2$ with Ln = La–Nd, Sm, Gd, and Tb

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Dedicated to Professor Mewis on the occasion of his 60th birthday

The 14 arsenides $LnAgAs_2$ and $LnAuAs_2$ (Ln = La–Nd, Sm, Gd, Tb) were prepared by reaction of stoichiometric mixtures of the elemental components at high temperatures and characterized by X-ray diffractometry. The silver compounds $LaAgAs_2$ and $CeAgAs_2$ and the gold compounds $LnAuAs_2$ (Ln = Ce–Nd, Sm, Gd, Tb) crystallize with $HfCuSi_2$ type structure ($P4/nmm$, Z = 2). Of these, the structures of $CeAgAs_2$ (a = 408.5(1), c = 1048.2(1) pm, conventional residual R = 0.017 for 261 structure factors and 12 variable parameters) and $CeAuAs_2$ (a = 411.4(1), c = 1015.3(2) pm, R = 0.030 for 428 F values) were refined from four-circle diffractometer data. The silver compounds $LnAgAs_2$ (Ln = Pr, Nd, Sm, Gd, Tb) are isotypic with the antimonide $SrZnSb_2$ ($Pnma$, Z = 4) as demonstrated by a single-crystal structure refinement of $PrAgAs_2$ (a = 2107.3(4), b = 401.7(1), c = 407.8(1) pm, R = 0.042 for 746 F values and 26 variables). The gold compound $LaAuAs_2$ ($I4/mmm$, Z = 4, a = 416.9(1), c = 2059.5(3) pm, R = 0.038 for 303 F values and 13 variables) was found to be isotypic with the bismuthide $SrZnBi_2$, again by a refinement from single-crystal diffractometer data. In the structures of $CeAgAs_2$, $LaAuAs_2$, and $CeAuAs_2$ large displacement parameters perpendicular to the four-fold axes were found for one of the two arsenic positions. These structures could also be refined with split positions for these arsenic atoms, which allow for considerable As–As bonding, resulting in a formal charge of -1 for these atoms. Chemical bonding in these compounds can thus be rationalized by a simple model corresponding to the formula $Ln^{+3}T^{+1}As^{-1}As^{-3}$ (T = Ag, Au), where the superscripts indicate oxidation numbers.

Key words: Rare Earth Compounds, Arsenides, Crystal Structure