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The new mineral baumstarkite and a structural reinvestigation of aramayoite and miargyrite

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ABSTRACT

Baumstarkite is a new mineral found coating miargyrite from the San Genaro mine, Huancavelica Department, Peru. It is triclinic and the third naturally occurring modification of $AgSbS_2$ besides monoclinic miargyrite and cubic cuboargyrite. The composition is usually close to the ideal formula. However, some grains of baumstarkite show zoned lamellae with As contents up to 11.5 wt% and accords to $Ag_3(Sb,As)_2SbS_6$. Baumstarkite is isotypic with aramayoite [end-member composition $Ag_3Sb_2BiS_6$; solid solutions require the extended formula $Ag_3Sb_2(Bi,Sb)S_6$]. Single-crystal X-ray structure investigations were performed for baumstarkite [type locality, a = 7.766(2), b = 8.322(2), c = 8.814(2) Å, α = 100.62(2), β = 104.03(2), γ = 90.22(2)°, $Z = 2\{Ag_3Sb_3S_6\}$, space group $P\bar{1}$, R1(F) = 0.057, $wR_2(F^2)$ = 0.128], aramayoite [Armonia mine, El Quevar, Argentinia: a = 7.813(2), b = 8.268(2), c = 8.880(2) Å, α = 100.32(2), β = 104.07(2), γ = 90.18(2)°, $Z = 2\{Ag_3Sb_2S_6\}$, space group $P\bar{1}$, R1(F) = 0.034, wR2(F^2) = 0.084], and miargyrite associated with baumstarkite type material [a = 12.862(3), b = 4.409(1), c = 13.218(3) Å, β = 98.48(2)°, $Z = 8\{AgSbS_2\}$, space group $C2/c$, R1(F) = 0.031, wR2(F^2) = 0.082]. The space-group symmetries of aramayoite and miargyrite were revised, and the refinements unambiguously showed that the three investigated minerals are centrosymmetric.

In baumstarkite and aramayoite each three atomic sites are occupied by Ag and M = As, Sb, Bi, respectively. The Ag atoms have two short bonded ligands (Ag-S is 2.51 to 2.58 Å). The M1 and M2 sites are [3 + 3] coordinated and are predominantly occupied by (Sb, As) atoms (M-S = 2.44 to 2.54 Å and > 3.09 Å). The [2 + 2 + 2] coordination of the M3 atom differs in the two mineral species: the two shortest bond lengths in baumstarkite are smaller (2.51 Å) than in aramayoite (2.64 Å) to allow for the different sizes of the Sb and Bi atoms, respectively; the medium bond lengths are similar (2.75 to 2.82 Å) and the longest bond lengths are >3.02 Å. Considering only the nearest-neighbor environments, baumstarkite and aramayoite feature zigzag chains parallel to [010], which are linked together to form layers parallel to (001). In miargyrite [2 + 2] and [2] coordinated Ag atoms are linked by SbS_3 pyramids to form a three-dimensional network.