

CRYSTAL STRUCTURE INVESTIGATIONS OF AgMS_2 MINERALS (M = As, Sb, Bi)

by

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Baumstarkite is a new mineral coating miargyrite from the San Genaro mine, Huancavelica Department, Peru. Baumstarkite is triclinic and is the third naturally occurring modification of AgSbS_2 besides monoclinic miargyrite [1,2] and cubic cuboargyrite [3]. The composition is usually close to the ideal formula. However, several grains of baumstarkite show sharply defined and chemically strongly zoned lamellae with As substituting for Sb according to $\text{Ag}_3(\text{Sb,As})_2\text{SbS}_6$ to a maximum As content of 11.5 wt.% (10.6 at.%). Baumstarkite is isotypic with aramayoite [4], ideally $\text{Ag}_3\text{Sb}_2\text{BiS}_6$, solid solutions are in accordance with $\text{Ag}_3\text{Sb}_2(\text{Bi,Sb})\text{S}_6$.

The crystal-structure investigation of baumstarkite is based on single-crystal X-ray data: $a = 7.766(2)$, $b = 8.322(2)$, $c = 8.814(2)$ Å, $\alpha = 100.62(2)$, $\beta = 104.03(2)$, $\gamma = 90.22(2)^\circ$, $Z = 2\{\text{Ag}_3\text{Sb}_3\text{S}_6\}$, space group $\text{P}\bar{1}$; $R1(F) = 0.057$, $\omega R2(F^2) = 0.128$. To facilitate the chemical separation of baumstarkite from aramayoite, and to enable a structural comparison with miargyrite the crystal structures of these two minerals were refined [samples of aramayoite came from the Mina Armonia, El Quevar, Argentina: $a = 7.813(2)$, $b = 8.268(2)$, $c = 8.880(2)$ Å, $\alpha = 100.32(2)$, $\beta = 104.07(2)$, $\gamma = 90.18(2)^\circ$, $Z = 2\{\text{Ag}_3\text{Sb}_2\text{BiS}_6\}$, space group $\text{P}\bar{1}$, $R1(F) = 0.034$, $\omega R2(F^2) = 0.084$; and the samples of miargyrite were those associated with baumstarkite type material, $a = 12.862(3)$, $b = 4.409(1)$, $c = 13.218(3)$ Å, $\beta = 98.48(2)^\circ$, $Z = 8\{\text{AgSbS}_2\}$, space group $\text{C}2/c$, $R1(F) = 0.031$, $\omega R2(F^2) = 0.082$]. Their space-group symmetries had to be revised, the refinements unambiguously showed that the three investigated minerals are centrosymmetric.

In baumstarkite, aramayoite, and miargyrite the surrounding of the Ag atoms is roughly characterized by the coordination numbers [2], [2+2], [4] or [2+2+2]. The gaps between the first and second coordination spheres differ but correlate with the shortest of the Ag–S bonds. Ag–S bond lengths start for $\text{Ag}^{[2]}$ atoms at 2.38 Å, for $\text{Ag}^{[2+2]}/\text{Ag}^{[4]}/\text{Ag}^{[2+2+2]}$ atoms between 2.51 and 2.54 Å. Additional S ligands exhibit a wide spread distribution of bond distances up to the same range as further cations. The S–Ag–S bond angles between the two nearest neighbours are 146° to 163° ; but for the $\text{Ag}_2^{[2]}$ atom in miargyrite the bond angle is 180° due to the site symmetry $\bar{1}$ of the central atom.

An analysis of the displacement parameters of the Ag atoms shows that their anisotropies correlate with the bond length distribution rather than with the S–Ag²⁺–S bond angles.

The M = As, Sb, Bi atoms exhibit two different coordination figures in minerals with formula AgMS₂. Most M atoms are [3+3] coordinated. The individual bond lengths M–S for the first coordination sphere are 2.44 to 2.54 Å (average bond lengths 2.463 to 2.492 Å). Next ligands have M–S > 3.09 Å. In baumstarkite and aramayoite, the positions M3 = Sb and Bi feature [2+2+2] coordination and a huge difference in the short M3–S bond lengths due to the predominant occupation by Sb and Bi atoms, respectively. The shortest and medium M3–S bond lengths in baumstarkite (~ 2.51 Å and 2.76 Å) are smaller than in aramayoite (~ 2.64 Å and 2.81 Å) to allow for the different size of the Sb and Bi atoms, respectively. Two further ligands are at a distance of ~ 3.0 Å indicating only moderate chemical interactions. It is worth mentioning that these fifth and sixth M3–S bond lengths are larger for baumstarkite than for aramayoite. This causes a stronger distortion for the M3S₆ polyhedron in baumstarkite (SbS₆) than in aramayoite (BiS₆). Probably steric reasons caused by the structure type are responsible for the reverse of the Bi–S / Sb–S bond lengths. In addition, the steric activity of the lone-pair electrons of the Sb³⁺ atoms seems to be more pronounced as compared to Bi³⁺ atoms.

The different size of the coordination of the M atoms reflects the chemical variability of baumstarkite and aramayoite. Despite ideal compositions of Ag₃Sb₃S₆ and Ag₃Sb₂BiS₆, extensive substitution between As / Sb and Sb / Bi was found by chemical analysis. Due to the different size and geometry of the M1^[3]S₃ and M2^[3]S₃ pyramids as compared to the M3^[2+2]S₄ polyhedra any significant As content substitutes for Sb at the M1 and M2 position whereas the M3 position is occupied either by Sb or by Bi atoms. Only small portions of Bi substituting for Sb at the M1 and M2 position in aramayoite were observed. Consequently the crystal chemical formula for the structure type is roughly Ag₃(As,Sb)₂(Sb,Bi)S₃. The compositions of baumstarkite and aramayoite are described as Ag₃(Sb,As)₂SbS₃ and Ag₃Sb₂(Bi,Sb)S₃, respectively. However, samples of baumstarkite with small contents of both As and Bi according to Ag₃(Sb_{0.95}As_{0.05})₂(Sb_{0.9}Bi_{0.1})S₃ were also detected.

Authors of the earlier papers dealing with X-ray work of AgMS₂ minerals have considered structural relations within this group of compounds and they mentioned the PbS type as the parental structure. Additionally, this structural relation is deduced from the phase transitions observed by the previous authors. Cubic high-temperature modifications of AgMS₂ are described as crystallizing in the PbS type; Ag and M atoms are octahedrally coordinated and occupy statistically one atomic site. The low-temperature modifications of these compounds exhibit a full order between Ag and M atoms accompanied by distinct coordinations. According to more detailed investigations of sulfosalts by [5] the type structure of the AgMS₂ minerals should be considered as derivatives of the SnS archetype to account for their special coordinations and the bond-strength distributions. Despite the derivation from one structure type, the linkage among the short connected atoms in the AgMS₂ minerals is quite different.

Considering only the nearest-neighbour environment the type structure of baumstarkite and aramayoite features zig-zag chains parallel to [010] with formula [AgMS₂]. The MS₃ pyramids are corner-connected to the MS₄ polyhedra. All Ag²⁺–S bonds are within the chains.

The chains are interlocked among each other by additional Ag–S and M–S bonds to layers parallel to (001). The Ag–S bonds between the layers are $> 2.93 \text{ \AA}$ and they are responsible for only weak chemical interactions. Miargyrite is formed by (MS₂) chains running parallel to [010] of corner connected SbS₃ pyramids. The chains are linked by Ag atoms. Comparing the cell volumes recalculated for one AgSbS₂ unit indicates distinct packing densities. Miargyrite (92.9 Å³) is less densely packed as compared to baumstarkite (90.3 Å³) and cubargyrite (90.2 Å³). It is worth mentioning that aramayoite has only a volume of 91.2 Å³ for one AgSb^{2/3}Bi^{1/3}S₂ unit, i.e., less than miargyrite. Structural data of the further minerals of the AgMS₂ group need a re-investigation: smithite, M = As [6], trechmannite, M = As [7], and matildite, M = Bi [8].

References

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