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Zinconigerite-2*N*1*S* $ZnSn_2Al_{12}O_{22}(OH)_2$ and zinconigerite-6*N*6*S* $Zn_3Sn_2Al_{16}O_{30}(OH)_2$, two new minerals of the nolanite-spinel polysomatic series from the Xianghualing skarn, Hunan Province, China

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Abstract

Zinconigerite-2*N*1*S* $ZnSn_2Al_{12}O_{22}(OH)_2$ and zinconigerite-6*N*6*S* $Zn_3Sn_2Al_{16}O_{30}(OH)_2$ are two new minerals with different numbers and ratios of nolanite (*N*) and spinel (*S*) modules. Both phases have been discovered in the Xianghualing skarn, Hunan Province, China. Zinconigerite-2*N*1*S* (zn-2*N*1*S*) and zinconigerite-6*N*6*S* (zn-6*N*6*S*) are named for their chemical composition, number, and ratios of *N*-*S* modules, according to the nomenclature of the nolanite-spinel polysomatic series of Armbruster (2002). Both phases occur as aggregates, sub-to-euhedral crystals, with maximal dimensions up to 100 μm, within fluorite aggregates, and they are closely associated with phlogopite, chrysoberyl, magnetite, cassiterite, margarite, and nigerite-taaffeite group minerals. They do not show fluorescence in long- or short-wave ultraviolet light. The calculated densities are 4.456 g/cm^3 for zn-2*N*1*S* and 4.438 g/cm^3 for zn-6*N*6*S*. Optically, zn-2*N*1*S* is uniaxial (+) with ω = 1.83(1), ε = 1.84(2); zn-6*N*6*S* is uniaxial (+) with ω = 1.85(1), ε = 1.87(2) (λ = 589 nm). Their chemical compositions by electron-microprobe analyses give the empirical formulas $(Zn_{0.734}Mn_{0.204}Na_{0.122}Ca_{0.063}Mg_{0.044})_{\Sigma 1.166}(Sn_{1.941}Zn_{0.053}Ti_{0.007})_{\Sigma 2}(Al_{11.018}Fe^{3+}_{0.690}Zn_{0.200}Si_{0.092})_{12}O_{22}(OH)_2$ for zn-2*N*1*S* and $(Zn_{1.689}Mn_{0.576}Mg_{0.328}Fe^{3+}_{0.407})_{\Sigma 3}(Sn_{1.882}Zn_{0.047}Ti_{0.071})_{\Sigma 2}(Al_{14.675}Fe^{3+}_{1.088}Na_{0.13}Ca_{0.086}Si_{0.017})_{\Sigma 15.996}O_{30}(OH)_2$ for zn-6*N*6*S*. Both phases have trigonal symmetry; the unit-cell parameters of zn-2*N*1*S* ($P\bar{3}m1$) and zn-6*N*6*S* ($R\bar{3}m$), refined from single-crystal X-ray diffraction data, are, a = 5.7191(2) and 5.7241(2) Å, c = 13.8380(6) and 55.5393(16) Å, V = 391.98(3) and 1575.96(12) Å^3, and Z = 1 and 3, respectively. The structure of zn-2*N*1*S* is characterized by the alternating O-T_1-O-T_2-O-T_1 layers stacked along the *c*-axis, showing the connectivity of *N*-*S*-*N*. The polyhedral stacking sequence of zn-6*N*6*S* is 3 × (O-T_1-O-T_2-O-T_2-O-T_1), reflecting a *N-S-S-N-N-S-S-N-N-S-S-N* connectivity of the polysomatic structure. By contrast, the structure of zn-2*N*1*S* shows the elemental replacements of Al → Sn and Al → Zn, suggesting the substitution mechanism of 2Al → Zn + Sn. The complex substitution of Zn by multiple elements (Al, Fe^{3+}, Mn, Mg) in the structure of zn-6*N*6*S*, is coupled with the low occupancy of Al5-octahedra. Fe^{3+} → Al substitution occurs in Al1-tetrahedra of both zn-2*N*1*S* and zn-6*N*6*S*. The new polysomes, zn-2*N*1*S* and zn-6*N*6*S*, likely crystallized under F-rich conditions during the late stages of the Xianghualing skarn formation. The discovery of zn-2*N*1*S* and zn-6*N*6*S* provides new insights into the crystal chemistry of the *N*-*S* polysomatic series and its origin.

Keywords: Zinconigerite-2*N*1*S*, zinconigerite-6*N*6*S*, nolanite module, spinel module, polysomatic series, Xianghualing skarn