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The crystal structure of esperite, with a revised chemical formula, $PbCa_2(ZnSiO_4)_3$, isostructural with beryllonite

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Abstract

Esperite from Franklin, New Jersey, was first described by Moore and Ribbe (1965) as monoclinic with a well-developed "superlattice" $a = 2 \times 8.814(2)$ Å, $b = 8.270(3)$ Å, $c = 2 \times 15.26(1)$ Å, $\beta \approx 90°$, space group $P2_1/n$ (subcell), and the chemical formula $PbCa_3(ZnSiO_4)_4$. They attributed "superlattice" reflections to the ordered distributions of Pb and Ca cations over four beryllonite-type subcells for esperite with the Ca:Pb ratio greater than 2:1.

We examined two esperite fragments from the type sample using single-crystal X-ray diffraction, electron microprobe analysis, and Raman spectroscopy. Although both fragments have Ca:Pb ≈ 1.8, one exhibits the "superlattice" reflections as observed by Moore and Ribbe (1965), whereas the other does not. The sample without "superlattice" reflections has unit-cell parameters $a = 8.7889(2)$, $b = 8.2685(2)$, $c = 15.254(3)$ Å, $\beta = 90.050(1)°$, $V = 1108.49(4)$ Å^3, and the chemical composition $Pb_{1.00}(Ca_{1.86}Fe^{2+}_{0.07}Mn_{0.04}Cr^{3+}_{0.02})_{\Sigma=1.99}(Zn_{1.00}Si_{1.00}O_4)_3$. Its crystal structure was solved in space group $P2_1/n$ ($R_1 = 0.022$). Esperite is isostructural with beryllonite, $NaBePO_4$, and its ideal chemical formula should, therefore, be revised to $PbCa_2(ZnSiO_4)_3$, Z = 4. The ZnO_4 and SiO_4 tetrahedra in esperite share corners to form an ordered framework, with Pb^{2+} occupying the nine-coordinated site in the large channels and Ca^{2+} occupying the two distinct octahedral sites in the small channels. The so-called "superlattice" reflections are attributed to triple twins, a trilling of ~60° rotational twinning around the *b* axis, similar to those observed in many other beryllonite-type materials. A phase transformation from a high-temperature polymorph to the esperite structure is proposed to be responsible for the twinning formation.

Keywords: Esperite, beryllonite, Pb-Zn silicates, crystal chemistry, X-ray diffraction