Molten Salt Fluxes, Polychalcogenide, Polyselenide

Na₂Ti₂Se₉ was first discovered in the quaternary system Na/Ti/P/Se, but it can be prepared rationally by dissolving Ti in a Na₂Seₓ flux at 375 °C. The silverish dark red crystals are air- and water-stable. A new method for synthesizing Na₄TiSe₄ is also reported. Na₂Ti₂Se₉ crystallizes in space group P2₁ with \( a = 12.785(4) \), \( b = 14.848(4) \), \( c = 13.961(4) \) Å, \( \beta = 94.556(4)^\circ \), \( R₁ = 0.0592 \) and \( wR₂ = 0.1336 \). The structure is similar to that of K₅NaTi₆Se₂₇. It contains infinite one dimensional chains which run parallel to the \( c \)-axis and contain Ti⁴⁺ centers bonded to Se₂²⁻ and Se²⁻ species. The \( 1/\infty[\text{Ti}_2(\text{Se}_2)_4\text{Se}]^{2-} \) chains pack together in a hexagonal pattern. All of the titanium atoms are surrounded by a pentagonal bipyramid of selenium atoms. The selenium atoms bridge the Ti centers in two different ways. Na₂Ti₂Se₉ is a semiconductor with a band gap, \( E_g \), of \( \sim 1.02 \) eV. The Raman spectra are also reported.