New Information on the Na-Ti-Se Ternary System

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$Na_2Ti_2Se_9$ was first discovered in the quaternary system Na/Ti/P/Se, but it can be prepared rationally by dissolving Ti in a Na_2Se_x flux at 375 °C. The silverish dark red crystals are air- and water-stable. A new method for synthesizing Na_4TiSe_4 is also reported. $Na_2Ti_2Se_9$ crystallizes in space group $P2_1$ with a = 12.785(4), b = 14.848(4), c = 13.961(4) Å, β = 94.556(4)°, $R1$ = 0.0592 and $wR2$ = 0.1336. The structure is similar to that of $K_5NaTi_6Se_{27}$. It contains infinite one dimensional chains which run parallel to the c-axis and contain Ti^{4+} centers bonded to Se_2^{2-} and Se^{2-} species. The $1/\infty[Ti_2(Se_2)_4Se]^{2-}$ 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. $Na_2Ti_2Se_9$ is a semiconductor with a band gap, E_g, of $\sim$ 1.02 eV. The Raman spectra are also reported.