Four stable new ternary compounds had been reported in the system Li$_2$O·CaO·SiO$_2$. (A.R. West, J. Am. Ceram. Soc. (1978) 61, No. 3-4) but no crystal chemistry was done on them. We grew crystals of the Li$_2$Ca$_2$SiO$_4$·$\alpha$ phase of optimum size for crystal structure analysis. Single crystal diffraction diagrams show the material to be triclinic, $P_1$, $a = 10.4530(10007)$, $b = 8.23120(10020)$, $c = 7.17000(0021)$, $\alpha = 77.7130(0024)$, $\beta = 90.0256(0023)$, $\gamma = 109.2640(0022)$. The structure was solved using 2166 observed reflections. Full matrix least squares refinement with anisotropic temperature factors was terminated when $R = 0.038$ and $R_p = 0.041$. In this structure the silicon in tetrahedral coordination forms two types of anions: a (Si$_4$O$_8$) unit like a zig-zag chain, and a (SiO$_2$)$^{2-}$ unit. The coordination polyhedra of the lithium is also a tetrahedron, but distorted, and joins together the two silicon anions, forming two-dimensional layers. The calcium has a distorted cube-like coordination polyhedron that links the silicon-lithium layers.