High-pressure and phase transitions in dalyite, a Zr-silicate

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Dalyite, ideally $K_2ZrSi_6O_{15}$, is a rare potassium zirconium silicate found as accessory phase in peralkaline granites and syenites, late-stage pegmatites, charoitites, lamproites, lamprophyres, fenites and carbonatites. Dalyite is known to provide useful insights on the geochemical composition of magmatic systems, since it is the stable Zr phase after zircon at high K_2O content and low Na_2O activity. Currently, the relationship among the Zr-bearing phases and their phase stability are still poorly constrained.

A natural single-crystal of dalyite with composition $(K_{1.74(8)}Na_{0.14(1)})(Zr_{0.92(3)}Ti_{0.01(1)})Si_{6.09(4)}O_{15}$ was recovered from the alkaline syenite of Agua de Pau (Sao Miguel, Azores), known to present a peculiar mineralogy (Nazzareni et al., 2019).

Dalyite symmetry is S.G. *P*-1, a = 7.37 Å, b = 7.73 Å, c = 6.91 Å, α = 106.2°, β = 111.5°, γ = 100.0°. Its structural evolution and compressibility were studied by *in-situ* single-crystal synchrotron X-ray diffraction up to 20.52(5) GPa. In the *P*-range investigated we observed: (*i*) a second order (distorsive) phase transition, from dalyite to dalyite-II (S.G. *P*-1), between 9.90(5) and 10.68(5) GPa, and (*ii*) a first-order phase transition, from dalyite-II to dalyite-III (S.G. *P*-1), between 11.06(5) and 12.03(5) GPa. Fitting the *PV* data with a second-order Birch–Murnaghan EoS (BM2) we obtained a value of K_{V0} = 51.4(4) GPa for dalyite (V_0 = 332.5(2)Å^3) and K_{V0} = 39(1) GPa for dalyite-III (V_0 = 670(4)Å^3); due to the narrow stability field of the dalyite-II polymorph (Å1.3 GPa) its elastic parameters could not be determined. The structure accommodates the deformation induced by pressure by increasing anisotropy, from dalyite having a strain ellipsoid axial value of ε_1:ε_2:ε_3~1.69:1.28:1 (calculated between 0.22(5) and 9.90(5) GPa) to dalyite-III with ε_1:ε_2:ε_3~6.4:2.0:1 (calculated between 12.03(5) and 20.52(5) GPa). Both phase transitions have been found perfectly reversible in character and the high-pressure polymorph structures have been solved. From dalyite to dalyite-II and dalyite-III the unit-cell doubled and the coordination of K polyhedra increases from eight-to nine-fold. Interestingly, before the first phase transition the SiO_4 tetrahedra have a significant role in accommodating the bulk compression and show different bulk compressibility (= 47(4) GPa, = 74(14) GPa and = 108(20) GPa), but after the transition the compressibility is accommodated mainly by deforming the ZrO_6 octahedra, the β-wollastonite chains and the 4- and 6-mRs tetrahedra rings The deformation of the SiO_4 tetrahedrons and Zr-polyhedrons constitutes a rather peculiar and unusual behaviour, rarely observed before in high-pressure studies.

Despite its rarity, dalyite records peculiar geochemical processes in peralkaline systems and the definition of the structure stability and single site elasticity constitute a novel valuable information for a better understanding of Zr partitioning in different classes of structures.

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