On the role of U/ThO$_8$ polyhedral distortions in controlling the high-pressure zircon->reidite type transition in U$_x$Th$_{1-x}$O$_4$

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Coffinite (USiO$_4$) and thorite (ThSiO$_4$) are conspicuous radiogenic silicates in the geonomy. They form U$_{1-x}$Th$_x$SiO$_4$ (uranotherite) solid solutions in zircon-type phase. Investigating the phase-evolution of these minerals is of utmost significance in realizing their applicability in the front-as well as at the back-end of nuclear industries and also from geological perspective, such as geochronology. We carried out a systematic study of zircon- to reidite-type (tetragonal I41/amd to I41/a) structural transitions of U$_{1-x}$Th$_x$SiO$_4$ solid solution, and investigated their mechanical behaviour. Our ab-initio calculations revealed a unique interconnection of phase transition pressure ($p_t$) with the change in U-Th concentration in the solid solution. The transition pressure is found to be minimum (6.82 GPa) for $x = 0.5$ whereas for the endmembers coffinite and thorite $p_t$'s are 8.52 and 8.68 GPa, respectively. We developed a novel method to estimate the longitudinal and angular distortions of the highly irregular U/ThO$_8$-triangular dodecahedra (snub-disphenoids). We have parameterized two new factors: $\delta$ (longitudinal distortions) and $\sigma^2$ (angular distortions) to quantify the polyhedral distortions. A detailed analysis of the snub-disphenoidal distortions demonstrates that the difference in angular distortion of UO$_8$ and ThO$_8$ polyhedra (i.e. $\sigma_{u}^2$ and $\sigma_{th}^2$) between zircon- and reidite-type phases becomes minimum when U and Th percentage are equal, leading to the structural phase transition at the minimum hydrostatic pressure for the unique chemical composition: U$_{0.5}$Th$_{0.5}$SiO$_4$. Our result is also substantiated by the minimum compressibility observed for the zircon-type U$_{0.5}$Th$_{0.5}$SiO$_4$. It is worthwhile to note that the distortions parameters, $\delta$ and $\sigma^2$ are defined without any attribute to external parameters. They
are also independent to the elements occupying the polyhedra. Thus, we propose that these parameters: $\delta$ and $\sigma^2$ can also be used to calculate the distortions of similar $AB_8$-type snub-disphenoids observed in zircon-, reidite-, fergusonite- and wolframite-type mineral phases.