

Relics of samarskite structure in a metamict ABO_4 mineral and its high-temperature transformations

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A mineral predetermined as samarskite and originating from Beinmyr, Norway, was found to be amorphous to X-rays. The chemical analysis yielded chemical formula $(REe_{0.381}Ca_{0.241}Fe_{0.207}U_{0.142})_{\Sigma 0.971}(Nb_{0.764}Ta_{0.262}Ti_{0.065})_{\Sigma 1.091}$ what fits quite well to the one of the assumed structural models for samarskite. Due to the mineral metamict nature, the structure recovery was induced by annealing experiments in air at 400, 500, 650, 800 and 1000°C. The sample portions were also heated in N_2 and in slightly reductive Ar/H_2 atmosphere at 600, 1000 and 1300°C. The annealing experiments in air showed the start of recrystallization at 650°C with crystallization of a pyrochlore phase and the occurrence of a new phase at 1000°C, which can be characterized as a proposed high-temperature samarskite phase with wolframite-type structure (s.g. $P2/c$, $a=5.63(1)$ Å, $b=9.93(2)$ Å, $c=5.19(1)$ Å, $\beta=93.6(2)^\circ$). The results of the annealing experiments in N_2 and Ar/H_2 atmosphere show similar recrystallization evolutions: at 600°C a pyrochlore phase recrystallizes and at 1000°C a new phase appears coexisting with previously recrystallized pyrochlore phase. At 1300°C the phases recrystallized at lower temperatures are still present and there is no indication of new phases or phase transitions. Different atmospheric conditions during recrystallization seem to influence the heating products since the high-temperature samarskite phase is observed only for the mineral heated in air. For N_2 and Ar/H_2 atmosphere beta-fergusonite seems to be the most probable high-temperature phase along with pyrochlore. The variability of recrystallization of samarskite should be attributed to complex chemical composition, stability of the original structure, annealing conditions and heavily metamictized crystal structure, thus imparting the identification of the original structure in the thermally untreated sample. TEM micrographs of the unheated samarskite evidence the preservation of the original structure fragments in predominantly amorphous mineral matrix. These crystalline domains show lattice fringes with d -values which could be assigned to a presumed low-temperature samarskite phase. SAED patterns obtained for the unheated sample confirmed these indications of the samarskite structure, which can be considered to be the original one. The patterns might be indexed obeying orthorhombic cell with $Pbcn$ space group and calculated unit cell parameters $a=5.69(2)$ Å, $b=4.91(2)$ Å, $c=5.21(2)$ Å. The low-temperature samarskite phase could be envisaged as a columbite-related structure assuming octahedral coordination for B-cations and octahedral or higher coordination for A-cations.