

REE-SUBSTITUTED Ca-FREE ZIRCONOLITES

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Zirconolite, nominal formula $\text{CaZrTi}_2\text{O}_7$, being typical of the Synroc ceramic proposed in Australia to immobilize high level radioactive waste (HLW) [1]. In the Synroc zirconolite is major host phase for actinides and zirconium. It can also incorporate minor rare earth (REE) and iron group elements (corrosion products). Major isomorphic substitutions in its lattice are: $\text{Zr}^{4+} = \text{An}^{4+}$, $\text{Ca}^{2+} + \text{Zr}^{4+} = 2(\text{An,REE})^{3+}$, and $\text{Ca}^{2+} + \text{Ti}^{4+} = (\text{An,REE})^{3+} + (\text{Al,Fe})^{3+}$, where $\text{An}^{3+/4+}$ – three- and tetravalent actinides. In the latter case complete REE and Al or Fe substitution for Ca and Ti produces REEZrTi(Al,Fe)O_7 formulation. This makes zirconolite suitable for incorporation of high amounts of REEs and corrosion products of HLW. Reference data on REE-substituted Ca free zirconolites are very limited. The phase with YZrTiAlO_7 formulation has been formerly synthesized [2]. We have found zirconolite with composition $(\text{Gd}_{0.90}\text{La}_{0.10})(\text{Zr}_{0.91}\text{Ce}_{0.13})(\text{Ti}_{1.20}\text{Al}_{0.69})\text{O}_7$ in one of the ceramics designed for immobilization of REE-actinide HLW fraction [3]. In this work we studied zirconolites with specified composition REEZrTiAlO_7 , where REE = La, Ce, Pr, Nd, Sm, Gd, Tb, and Y.

To produce samples oxide mixtures were milled in an AGO-2U planetary mill / activator, compacted in pellets at 200 MPa followed by sintering at 1450 °C or melting at 1550 °C in air. To convert Ce (IV) to Ce (III) one test was performed under reducing conditions (carbon was introduced in batches). The ceramics were examined with X-ray diffraction (XRD), scanning (SEM) and transmission electron microscopy (TEM).

From XRD data the La-, Ce-, Pr-, and Nd-bearing samples were not single-phase ceramic. The La-bearing sample was composed of major perovskite-type phase and minor baddeleyite. The Ce-bearing samples consisted of major pyrochlore, cerianite-zirconia based cubic solid solution as a second in abundance phase, and minor zirconolite. The Pr-bearing ceramic contained major baddeleyite and perovskite-type phase, and minor pyrochlore. In the Nd-, Sm-, Gd-, Tb-, and Y-bearing samples zirconolite was predominant. Using SEM in the Nd-, Sm, and Y-bearing ceramics rare grains of REE-stabilized zirconia (fianite) have been found. The Gd- and Tb-bearing samples were single phase. Average zirconolite formulae were found to be $\text{Sm}_{1.06}\text{Zr}_{1.07}\text{Ti}_{1.00}\text{Al}_{0.86}\text{O}_7$, $\text{Gd}_{1.01}\text{Zr}_{1.05}\text{Ti}_{0.98}\text{Al}_{0.95}\text{O}_7$, $\text{Tb}_{0.93}\text{Zr}_{1.09}\text{Ti}_{1.08}\text{Al}_{0.85}\text{O}_7$, and $\text{Y}_{1.05}\text{Zr}_{1.03}\text{Ti}_{1.03}\text{Al}_{0.87}\text{O}_7$ that is close to specified zirconolite formula within experimental error.

XRD patterns of the Tb- and Y-bearing zirconolites are typical of zirconolite-2M variety. XRD patterns of the Nd-, Sm-, and Gd-bearing zirconolites differ from patterns typical of 2M, 3T, and 3O varieties known from reference data [4]. TEM study shows probable tetragonal symmetry of the zirconolite lattice on electron diffraction pattern.