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Effects of ionizing radiation on the hollandite structure-type: $Ba_{0.85}Cs_{0.26}Al_{1.35}Fe_{0.77}Ti_{5.90}O_{16}$

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Abstract

The hollandite structure-type has received considerable attention as a nuclear waste form for the incorporation of radioactive ^{135}Cs and ^{137}Cs, both of which are important fission product radionuclides in the high-level nuclear waste generated by the reprocessing of used nuclear fuel. A critical concern has been the effects of high doses of ionizing radiation from incorporated Cs on the long-term structural stability of the hollandite structure. Optimization of the synthesis conditions has resulted in the hollandite stoichiometry of $Ba_{0.85}Cs_{0.26}Al_{1.35}Fe_{0.77}Ti_{5.90}O_{16}$. To evaluate the effect of Cs-beta-decay on this stoichiometry, we have simulated the ionizing radiation using 200 kV electron beam using transmission electron microscopy (TEM) at 298 and 573 K. Complete amorphization was achieved at doses of 1.1×10^{14} and 1.8×10^{14} Gy at temperatures of 298 and 573 K, respectively. Electron energy-loss spectroscopy (EELS) of the Cs *M*-edge revealed the selective loss of Cs at the maximum doses. Hollandite irradiated using gamma rays, ~10^6 Gy, which has defects associated with the formation of Ti^{3+} and O_2^- had a dissolution rate similar to that of the pristine hollandite, suggesting that the initial stage of defect formation does not influence chemical durability. Because the accumulated dose in the hollandite with 5 wt% of radioactive $^{137}Cs_2O$ is estimated to be ~2.0×10^{10} Gy after 500 years, the hollandite structure should be stable under the conditions anticipated for geologic disposal.

Keywords: Hollandite, ionizing radiation, TEM, cesium, beta-decay