SAND2018-11848C

Title: Synthesis and processing of meta-stable negative thermal expansion materials $Zr_2WP_2O_{12}$ and ZrW_2O_8 as a wasteform

Abstract:

Although thermal expansion is the rule, a select subclass of materials exists that contracts under thermal stress – so called negative thermal expansion (NTE) materials. Many of these materials exhibit anisotropic negative thermal expansion – contraction in one or two dimensions with expansion in the third. This characteristic typically is limited to a narrow temperature range. Zirconium tungstate (ZrW_2O_8) is among the few known materials exhibiting isotropic negative thermal expansion over a broad temperature range, including room temperature where it crystallizes in the acentric cubic α-ZrW_2O_8 phase. Isotropic NTE materials are important for technological applications requiring thermal-expansion compensators in composites designed to have overall zero or adjustable thermal expansion. Two characteristics of ZrW_2O_8 and $Zr_2WP_2O_{12}$ are important for this work – both can accommodate substitution, and secondly these materials contract upon amorphization which means that metamictization would not cause damaging expansion. Fabrication of a wasteform with a shell of an NTE material such as ZrW_2O_8 and $Zr_2WP_2O_{12}$ and a core of radionuclide substituted material would potentially limit the radiation damage due to radionuclide release.

The phases of ZrW_2O_8 and $Zr_2WP_2O_{12}$ that display negative thermal expansion are stable to >950 K and to >1600 K respectively, with coefficients of thermal expansion of -8.8×10^{-6} K^{-1} and -6×10^{-6} K^{-1}.1, 2 In this work, we have adapted solution routes in a new fashion using a PTFE Teflon™ pouch to synthesize ZrW_2O_8 and its phosphorous analog $Zr_2WP_2O_{12}$. The characterized phase pure products were then sintered into pellets using spark plasma sintering. This process uses a current to resistively heat the sample while applying high pressure. A sintering protocol to maintain phase purity while achieving high densification was identified for both materials, with that for $Zr_2WP_2O_{12}$ employing 60MPa of pressure at 1400 C. Scanning Electron Microscopy, Powder X-ray diffraction, pycnometry, Raman spectroscopy and Fourier transform Infrared Spectroscopy were used to corroborate density, morphology and phase results.

Ref:

1. A. P. Wilkinson, C. Lind, S. Pattanaik, Chem. Mater. 1999 11, 101-108.
2. J.S.O Evans, T. A Mary, and A. W. Sleight, J. solis State Chem. 1997, 133, 580-583.