A 23Na Magic Angle Spinning Nuclear Magnetic Resonance, XANES, and High Temperature X-Ray Diffraction Study of NaUO3, Na4UO5, and Na2U2O7

Abstract:
The valence state of uranium has been confirmed for the three sodium uranates, NaU(V)O3/[Rn](5f1), Na4U(VI)O5/[Rn](5f0), and Na2U2O7/[Rn](5f0), using X-Ray Absorption Near-Edge Structure (XANES) spectroscopy. Solid state 23Na Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) measurements have been performed for the first time, yielding chemical shifts at -29.1 ppm (NaUO3), 15.1 ppm (Na4UO5), and -14.1 and -19 ppm (Na1 8-fold coordinated and Na2 7-fold coordinated in Na2U2O7), respectively. The [Rn]5 f 1 electronic structure of Uranium in NaUO3 causes a paramagnetic shift compared to Na4UO5 and Na2U2O7, where the electronic structure is [Rn]5 f 0. A 23Na Multi Quantum Magic Angle Spinning (MQMAS) experiment performed on Na2U2O7 has also confirmed a monoclinic rather than rhombohedral structure (Gasperin 1986) with the evidence of two distinct Na sites. DFT-NMR calculations of the NMR parameters have moreover been performed on the non magnetic compounds Na4UO5 and Na2U2O7, allowing the differentiation between the two Na sites of the Na2U2O7 structure. The linear thermal expansion coefficients of all three compounds have been determined using high temperature X-Ray diffraction: alpha_a = 22.7*10−6K−1, alpha_b = 12.9*10−6K−1, alpha_c = 16.2*10−6K−1 and alpha_vol = 52.8*10−6K−1 for NaUO3 in the range 298-1273 K; alpha_a = 37.1*10−6K−1 , alpha_c = 6.2*10−6K−1 and alpha_vol = 81.8*10−6K−1 for Na4UO5 in the range 298-1073 K; alpha_a = 6.7*10−6K−1 , alpha_b = 114.4*10−6K−1, alpha_c = 26.8*10−6K−1, alpha_b = −7.8* 10−6K−1 and alpha_vol = −217.6* 10−6K−1 for Na2U2O7 in the range 298-573 K. The alpha to beta phase transition reported for the latter compound above about 600 K (Cordfunke et al. 1982) was not observed in the present studies, either by high temperature X-Ray diffraction or by differential scanning calorimetry.

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