Physical properties of Ti-doped sodium alanates: First-principles studies and experiments
VIDVUDS OZOLINS, Dept. of Materials Science and Engineering, University of California, Los Angeles, CA 90095-1595

The recent surge in research on sodium alanates, NaAlH$_4$ and Na$_3$AlH$_6$, has been motivated by Bogdanovic’s discovery that, when doped with small amounts of Ti, these compounds can reversibly store more than 4 wt.% hydrogen. The location of catalytically active Ti and the mechanisms of enhanced H$_2$ sorption kinetics are still poorly understood. We will report on combined first-principles and experimental studies of structural, thermophysical and lattice dynamical properties of bulk alanates. Polarized Raman scattering on single crystals of NaAlH$_4$ has been used to determine the frequencies of the Raman-active vibrational modes between 300 and 425 K, i.e., up to the melting point $T_m$. Significant softening (by up to 6%) is observed in the modes involving rigid translations of Na$^+$ cations and translations and librations of AlH$_4^-$ tetrahedra. Surprisingly, less than 1.5% softening is seen for the Al-H stretching and Al-H bending modes, indicating that the AlH$_4^-$ anion remains a stable structural entity even near $T_m$. The phonon mode Grüneisen parameters, calculated using the quasiharmonic approximation, are found to be significantly higher for the translational and librational modes than for the Al-H bending and stretching modes, but cannot account quantitatively for the dramatic softening observed near $T_m$, suggesting an essentially anharmonic mechanism. The calculated lattice expansion due to zero-point vibrations is found to be large (1.2 and 1.5% for the $a$ and $c$ parameters, respectively), as expected for a compound with many light elements. The formation energies of Ti impurities in bulk alanates are found to be high (>1 eV), indicating that bulk substitution should not occur under normal conditions. We discuss the implications of these results for the kinetics of hydrogen release and hypothesize that breaking up the AlH$_4^-$ anions is the rate limiting step. The enhanced kinetics in Ti-doped NaAlH$_4$ powders is attributed to the effectiveness of Ti in promoting the break-up of the AlH$_4^-$ anions at the interface between NaAlH$_4$ and Na$_3$AlH$_6$. 