**Computational and experimental reinvestigation of**

**the structural and electrolyte properties of Na4P2S6 and Li4P2S6\***

**Yan Li and N. A. W. Holzwarth**

**Department of Physics, Wake Forest University, Winston-Salem, NC, 27109, USA**

Recent experiments1,2 have shown that Na4P2S6 crystalizes in the based-centered monoclinic structure C2/m (#12) and has good ionic conductivity and stability with respect to metallic Na anodes. However, previous simulations3 suggested that the monoclinic structure initially reported by Kuhn *et al*.2 is meta-stable relative to structures found for the similar material Li4P2S6. Our results in this extended work indicate that the vibrational free energy contributes to the stabilization of the C2/m structure of Na4P2S6. In modeling ionic conductivity in Na4P2S6, the calculated activation energy for Na ion migration is in reasonable agreement with the experimentally measured value.1 By using a combination of NMR and X-ray analysis, Neuberger *et al.*4 observed that the Li4P2S6 crystallizes to form an ordered hexagonal crystal having the space group P321 (#150). Our simulations of crystalline Li4P2S6, including both structural optimization and vibrational free energy contributions, are also consistent with this new structural analysis.

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1Z. D. Hood et al., to be published.

2A. Kuhn et al., Z. Anorg. Allg. Chem., **640**, 689–692 (2014)

2E. Rush Jr. et al., Solid State Ionics, **286**, 45-50 (2016).

4S. Neubergeret al. Dalton Transactions, **47**, 11691-11695 (2018).