We report high temperature inelastic neutron scattering measurements on Li2O [1], LiAlSiO4 [2], LiAlO2, LiFePO4 and LiMnPO4 [3] to understand its vibrational and thermodynamic behavior. The temperature dependent phonon spectra show a complete disappearance of some of the vibrational peaks at high temperatures. The calculated phonon spectra using ab-initio density functional theory implies that the disappearing peaks in these compounds are the vibrational modes of Li. The displacement pattern of the soft modes indicate possible pathways for Li diffusion. Molecular dynamics calculations of the phonon spectra at high temperature reproduced the behaviour observed experimentally.

The calculated energy barriers in LiAlSiO4 shows a highly anisotropic Li diffusion along hexagonal c-axis accompanied by inter- and intra-channel correlated motion of Li in the channels with activation energy of ≈0.3 eV. The calculated diffusion coefficient for Li atoms shows the 1-D superionic conductivity in LiAlSiO4 above 1000 K. On the other hand, in LiAlO2, higher activation energy of 0.9 eV for Li diffusion implies a lower ionic conductivity and higher conduction temperature as compared to that in LiAlSiO4.

We have also studied the anisotropic negative thermal expansion along c-axis [2] in LiAlSiO4 and identified the phonon modes governing this type of behaviour. The anisotropic Grüneisen parameters along with anisotropic elastic constants give rise to anisotropy in thermal expansion behaviour of LiAlO2 and LiAlSiO4.

The compounds LiMPO4 (M=Fe, Mn) do not show fast ion diffusion unless doped. Our Molecular dynamics studies at high temperatures indicate that the compound is stable up to 1000 K [3].

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