Supplementary Information (SI) for New Journal of Chemistry.

Theoretical investigation of the functional and photocatalytic properties of Li_2TiX_6 (X = Cl, Br, I) double perovskites using Density Functional Theory

Lalrin Puia,[a,b] Laltha kimi,[a,b] Angela Chinggelkim,[a,b] R. Zosiamliana,[a,b] Lalhum Hima,[a,b] Celestine Lalengmawia,[a,b] Lalrin Thara,[a] Shivraj Gurung,[a] and Lalhriat Zuala*[a]

[a] *Physical Sciences Research Centre (PSRC), Department of Physics, Pachhunga University College, Aizawl, 796001, India,*

[b] *Department of Physics, Mizoram University, Aizawl, 796004, India*

* *Email:hriatamail@gmail.com*

Phonon calculation:

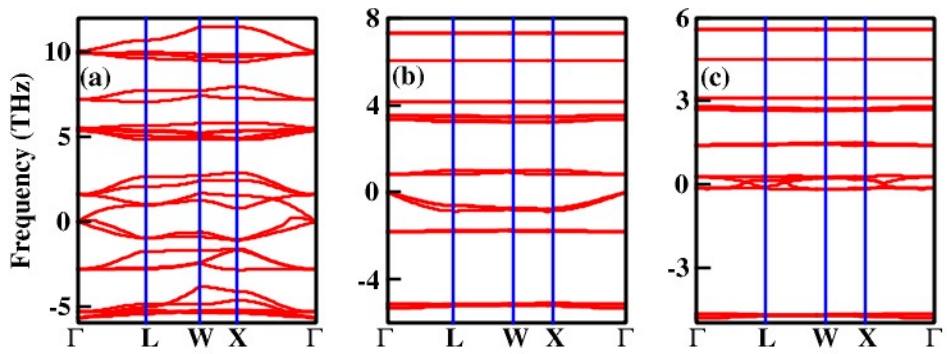

Figure S1: Phonon dispersion (a) Li_2TiCl_6 , (b) Li_2TiBr_6 and (c) Li_2TiI_6

The calculated phonon dispersion curves for the cubic phase given in the Figure S1, exhibit soft-mode instabilities, characterized by imaginary frequencies. These modes signify a dynamical instability of the Fm $\bar{3}$m symmetry at 0K, a hallmark of vacancy-ordered double perovskites (VODPs) where the high-symmetry framework is often a saddle point on the potential energy surface. Physically, these instabilities correspond to symmetry-breaking displacive transitions, typically driven by the collective tilting of BX_6 octahedra or subtle distortions within the vacancy-ordered sublattice (Mahi et al., 2024). While these negative branches suggest instability in a static 0K limit, they are frequently renormalized by anharmonic effects at finite temperatures as demonstrated by Chen et al. using the Temperature-Dependent Effective Potential (TDEP) method (Hellman et al., 2013), the inclusion of anharmonic phonon renormalization (APRN)(Guo & Guo, 2023) can effectively stabilize such frameworks (Chen et al., 2024). Similar behaviour has been noticed in Cs_2SnX_6 (X = Br, I) and Cs_2MoI_6, where imaginary components observed at 0 K vanish under ambient conditions as we increase the temperature, this confirms the material's structural integrity at room temperature(Jong et al., 2019, 2022) (Ahmed et al., 2023). Furthermore, research by Faizan et al. reinforces that these T= 0K instabilities are often artifacts of neglecting thermal expansion and ionic fluctuations, both of which restore dynamical stability at T = 300 K (Faizan et al., 2022). Consequently, the observed soft modes in our system are indicative of a temperature-driven phase stabilization rather than a fundamental lack of structural viability.

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