

Supplementary Information

Unusual terahertz-wave absorptions in δ - and α -phase mixed FAPbI₃ single crystal: Interfacial phonon vibration modes

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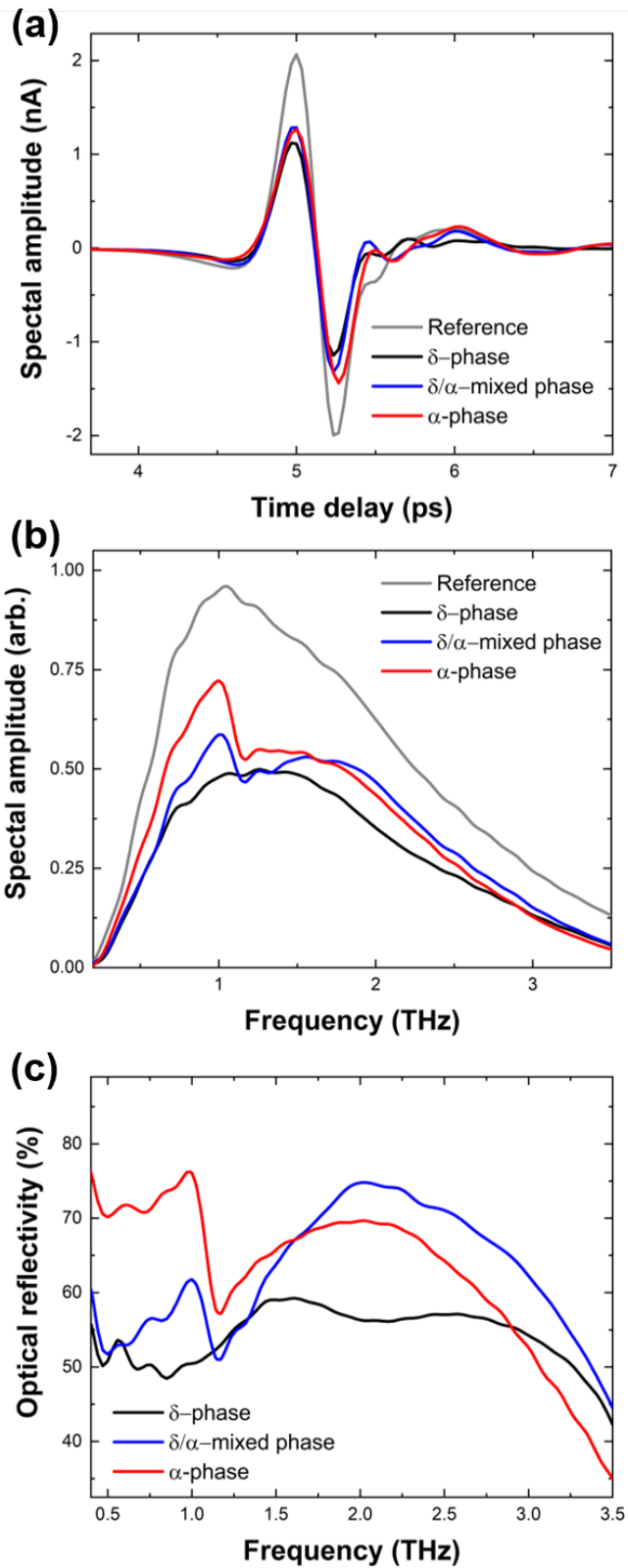


Figure S1. (a) THz time domain waveforms obtained from our THz time domain spectroscopy comparing the gold coated planar mirror (gray line) (b) THz frequency domain waveforms using Fourier transformations (c) optical reflectivity of the samples.

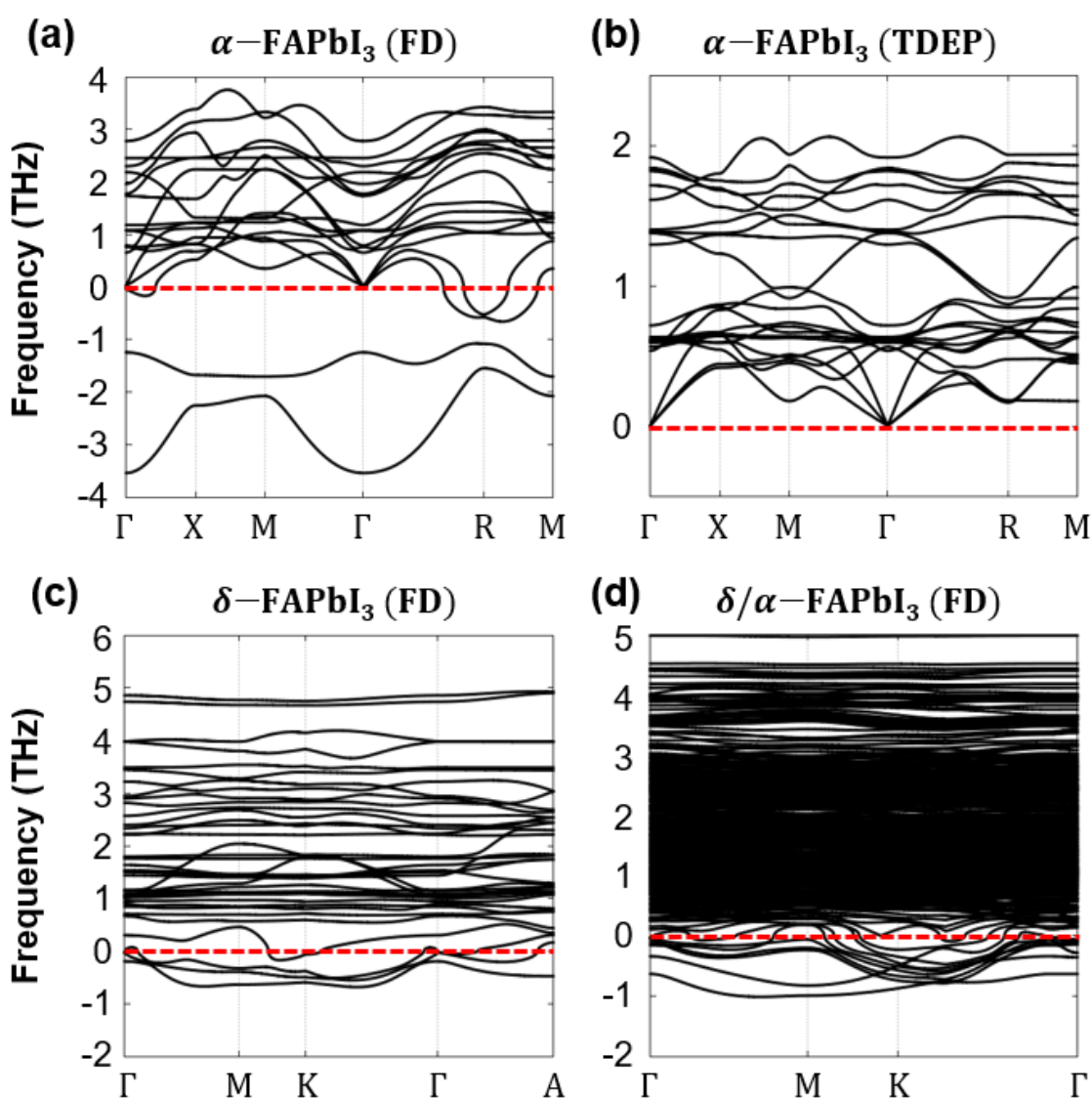


Figure S2. Phonon dispersion relations of (a, b) α -FAPbI₃ calculated by the finite displacement (FD) method (a) and the temperature-dependent effective potential (TDEP) approach (b), (c) δ -FAPbI₃, and (d) their δ/α mixture phase calculated by the FD method. The red dashed lines indicate the zero phonon frequencies.

Supplementary Note

It is known that the phonon dispersion relation for high-temperature phases of OHP cannot be described well by a finite displacement (FD) method since the FD method cannot incorporate the dynamic effect of organic molecules. Our previous study [S1] revealed that these dynamic effects could be properly described by the temperature-dependent effective potential (TDEP) approach. Figures S1(a) and (b) show the phonon dispersion relations calculated by the conventional finite displacement (FD)

method and TDEP approach, respectively. The former exhibits a large number of unphysical phonon modes with imaginary frequencies owing to the freely rotating FA molecules. In contrast, the TDEP result shows a phonon dispersion relation without any imaginary modes.

Conversely, for low-temperature phases of OHP, such as an orthorhombic or tetragonal phase, the FD method still guarantees sufficiently good phonon dispersion relations given that the organic molecules are relatively stationary rather than dynamically rotating owing to their insufficient kinetic energies [S2]. Nevertheless, δ -FAPbI₃ is still not the zero-temperature phase of FAPbI₃ [S3]. Thus, in principle, it would be necessary to apply the TDEP method for its accurate phonon properties. Unfortunately, we could not apply the TDEP method for δ -FAPbI₃ because a huge amount of computational resources is required to calculate its finite-temperature force constants matrix owing to its relatively large unit cell structure with low symmetry. Instead, we applied the FD method to evaluate its phonon dispersion relation shown in Fig. S1(c). Despite these limitations, we found that the FD method can provide a reasonable result to understand the physical properties of the δ -phase because its distorted inorganic lattice restricts the free vibrations of FA molecules unlike in the α -phase.

For the mixture phase, we tried to construct a sufficiently large unit cell with which we can rule out an artificial effect from a short periodicity along the [0001] direction. The structure shown in Fig. 5(c) is the largest cell we can deal with in our computational resources, but it is clear that the unit cell size is not large enough to fully incorporate the experimental measurement, including contributions from the unmixed δ - and α -phases and their interfaces. Nevertheless, we believe that this model unit cell structure can reflect at least the interface between two unmixed phases and the limited rotation of FA molecules owing to the additional strain at the interface. Therefore, it is reasonable that the FD method is still valid in calculating the phonon properties of the mixture phase.

References

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- [S3] B. Kim, J. Kim, and N. Park, *First-Principles Identification of the Charge-Shifting Mechanism and Ferroelectricity in Hybrid Halide Perovskites*, Sci. Rep. **10**, 1 (2020).