Supplementary Information for "Machine Learning Modeling of Temperature-Dependent Optoelectronic Properties of Anharmonic Solid Solutions"

Pol Benítez and Cibrán López

Department of Physics, Universitat Politècnica de Catalunya, Barcelona 08019, Spain and

Research Center in Multiscale Science and Engineering,

Universitat Politècnica de Catalunya, 08019 Barcelona, Spain

Edgardo Saucedo

Research Center in Multiscale Science and Engineering,

Universitat Politècnica de Catalunya, 08019 Barcelona, Spain and

Departament d'Enginyeria Electrònica,

Universitat Politècnica de Catalunya, 08034 Barcelona, Spain

Claudio Cazorla

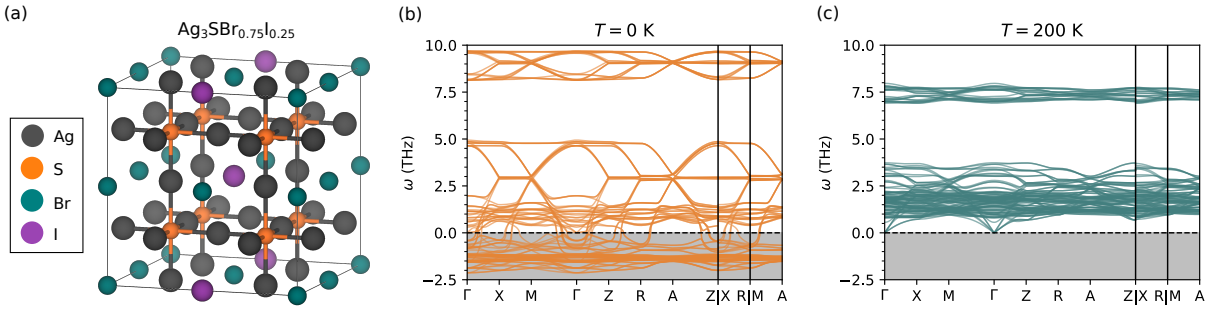
Department of Physics, Universitat Politècnica de Catalunya, Barcelona 08019, Spain

Research Center in Multiscale Science and Engineering,

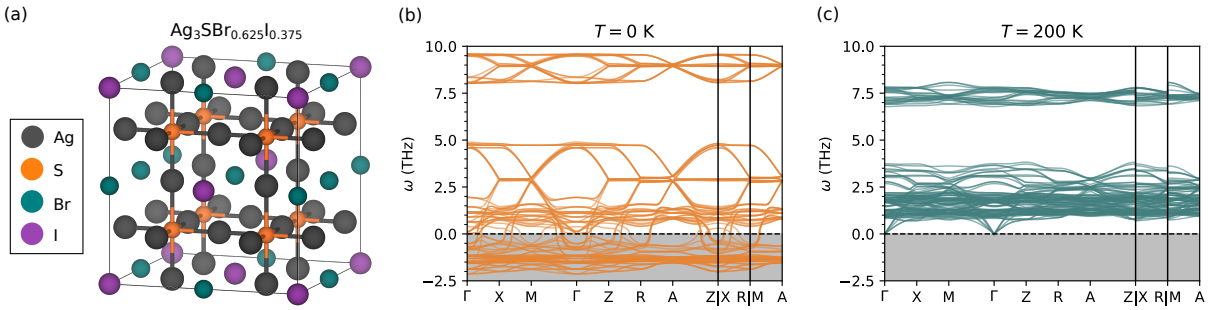
Universitat Politècnica de Catalunya, 08019 Barcelona, Spain and

Institució Catalana de Recerca i Estudis Avançats (ICREA),

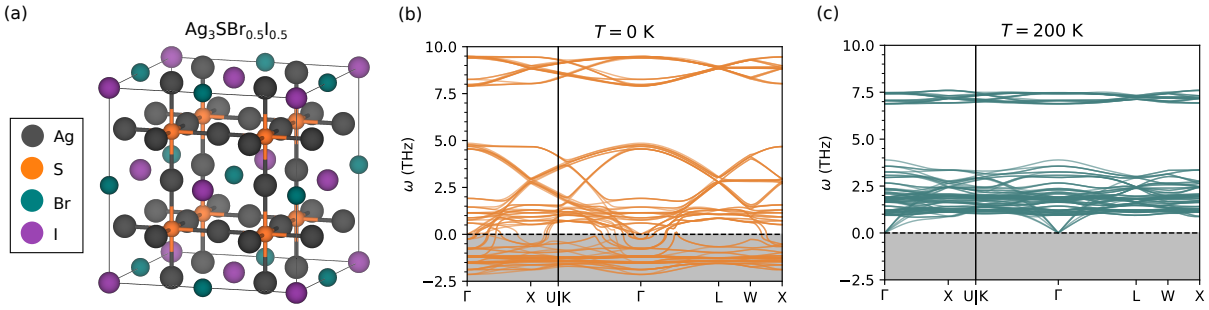
Passeig Lluís Companys 23, 08010 Barcelona, Spain



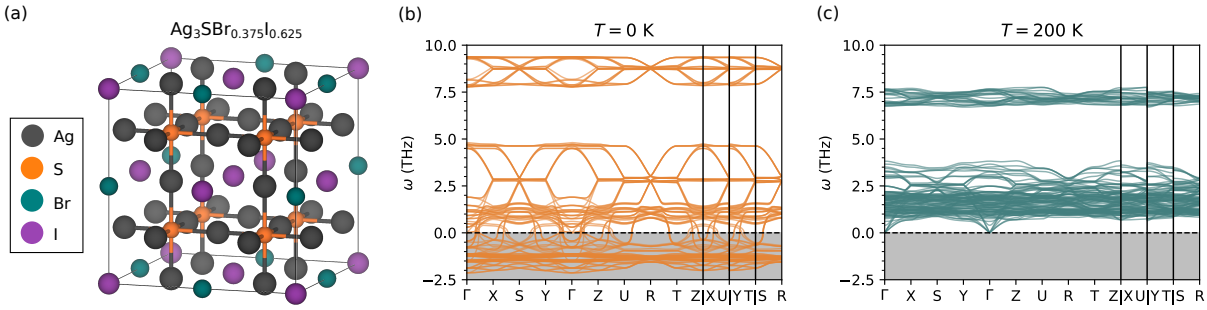
Supplementary Figure 1: (a) Representation of the equilibrium structure determined for the solid solution $Ag_3SBr_{0.75}I_{0.25}$. Phonon dispersions calculated at (b) zero temperature, and (c) at $T = 200$ K.



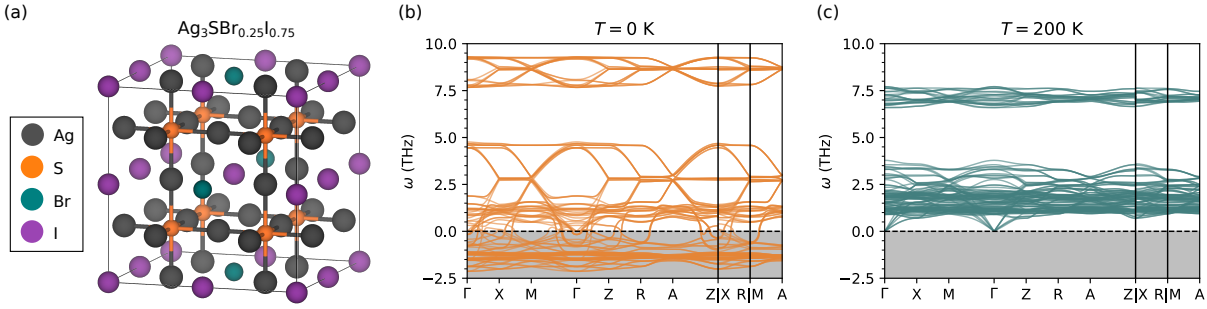
Supplementary Figure 2: (a) Representation of the equilibrium structure determined for the solid solution $Ag_3SBr_{0.625}I_{0.375}$. Phonon dispersions calculated at (b) zero temperature, and (c) at $T = 200$ K.



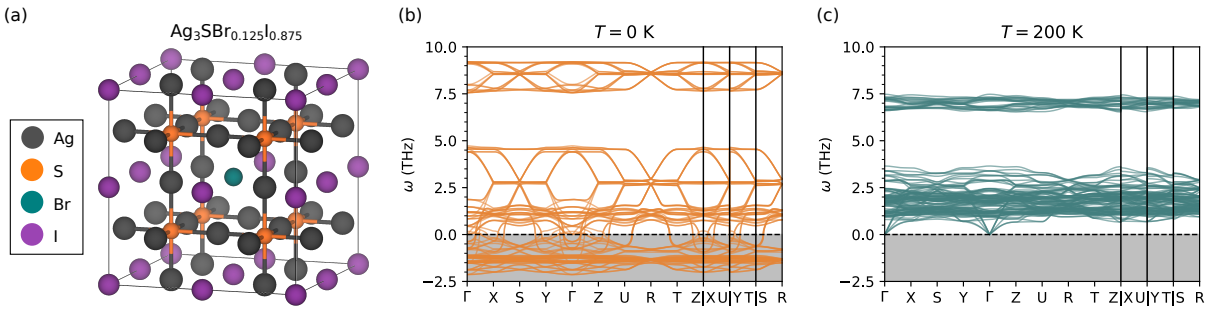
Supplementary Figure 3: (a) Representation of the equilibrium structure determined for the solid solution $Ag_3SBr_{0.5}I_{0.5}$. Phonon dispersions calculated at (b) zero temperature, and (c) at $T = 200$ K.



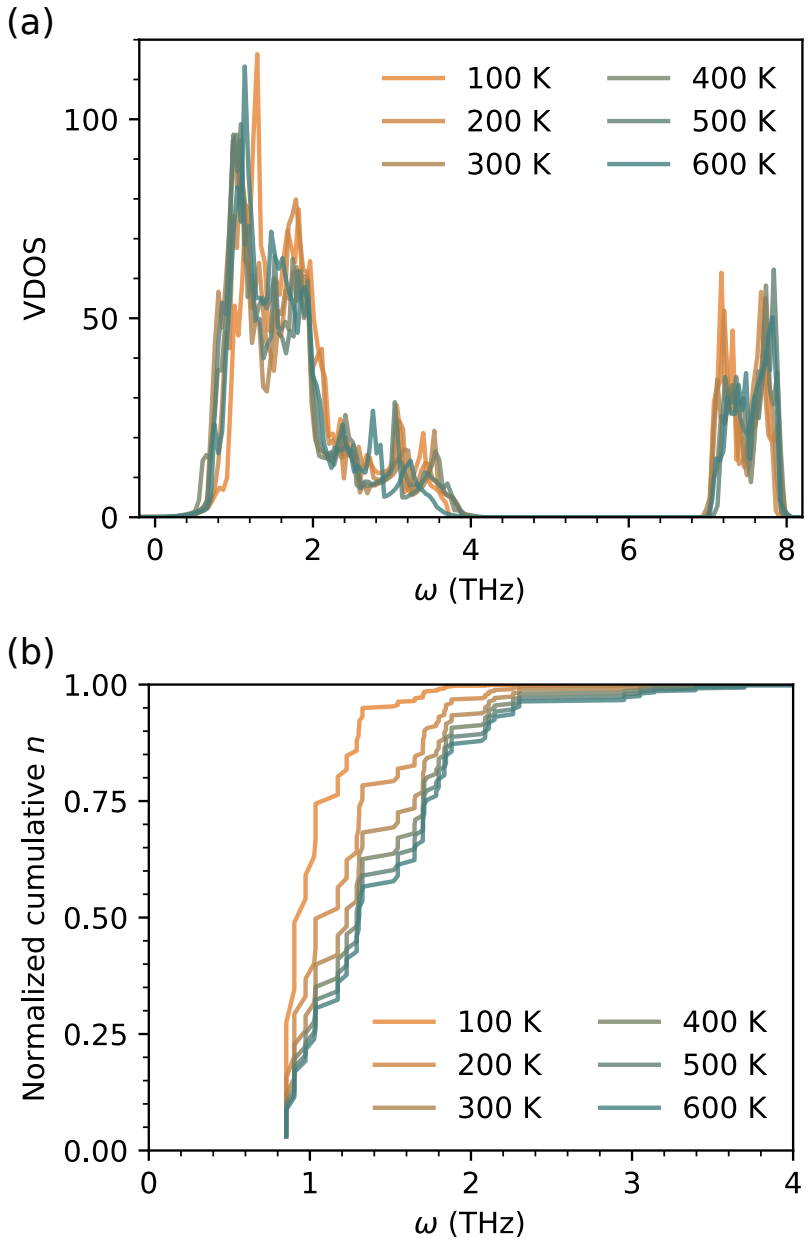
Supplementary Figure 4: (a) Representation of the equilibrium structure determined for the solid solution $Ag_3SBr_{0.375}I_{0.625}$. Phonon dispersions calculated at (b) zero temperature, and (c) at $T = 200$ K.



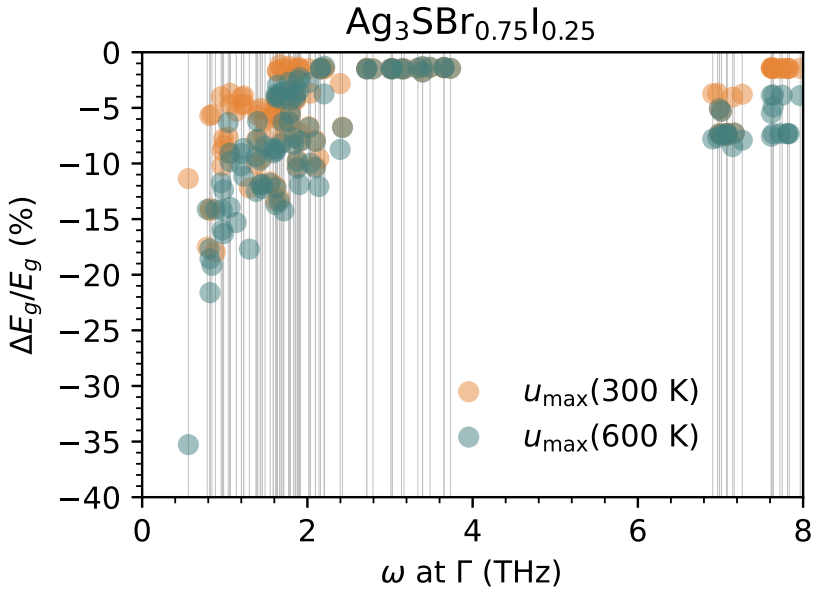
Supplementary Figure 5: (a) Representation of the equilibrium structure determined for the solid solution $Ag_3SBr_{0.25}I_{0.75}$. Phonon dispersions calculated at (b) zero temperature, and (c) at $T = 200$ K.



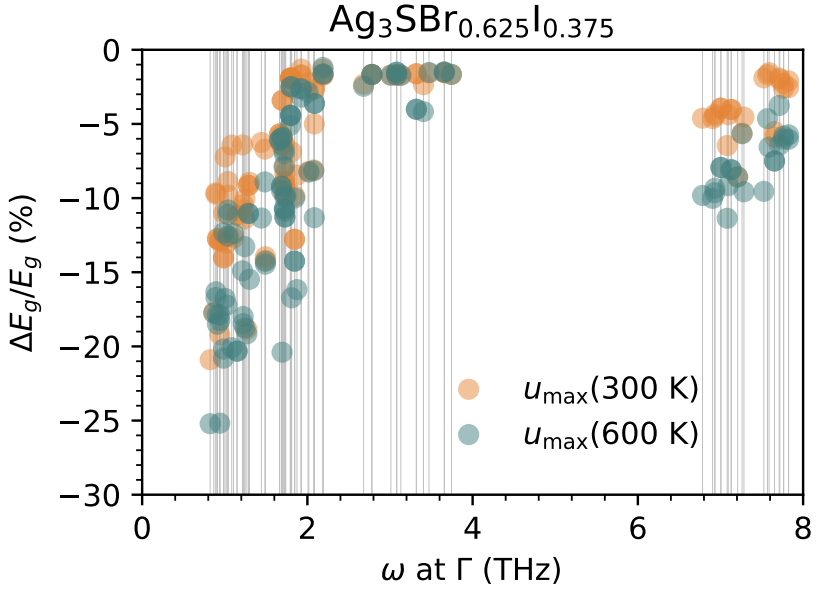
Supplementary Figure 6: (a) Representation of the equilibrium structure determined for the solid solution $Ag_3SBr_{0.125}I_{0.875}$. Phonon dispersions calculated at (b) zero temperature, and (c) at $T = 200$ K.



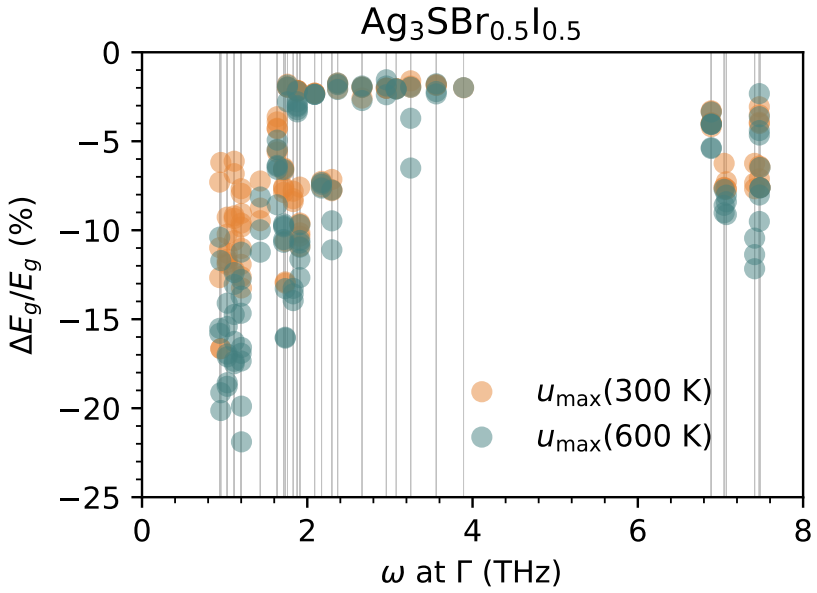
Supplementary Figure 7: (a) Temperature-dependence of the vibrational density of states (VDOS). T-renormalised VDOS were calculated by performing Fourier transform of the velocity autocorrelation function obtained from molecular dynamics simulations. (b) Normalized cumulative VDOS occupation for the solid solution $Ag_3SBr_{0.875}I_{0.125}$ (considering Γ-point phonons only).



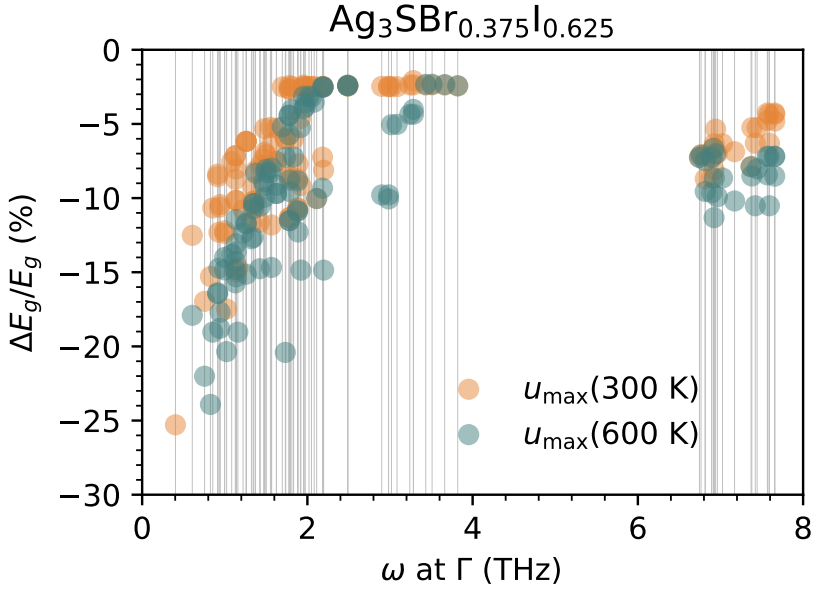
Supplementary Figure 8: Predicted relative band-gap change upon Γ-phonon mode distortions at 300 and 600 K for $Ag_3SBr_{0.75}I_{0.25}$.



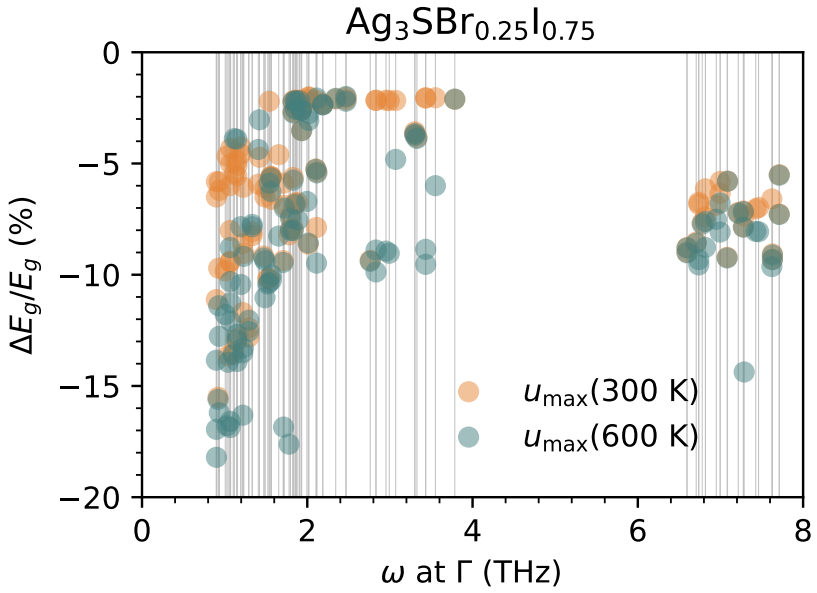
Supplementary Figure 9: Predicted relative band-gap change upon Γ-phonon mode distortions at 300 and 600 K for $Ag_3SBr_{0.625}I_{0.375}$.



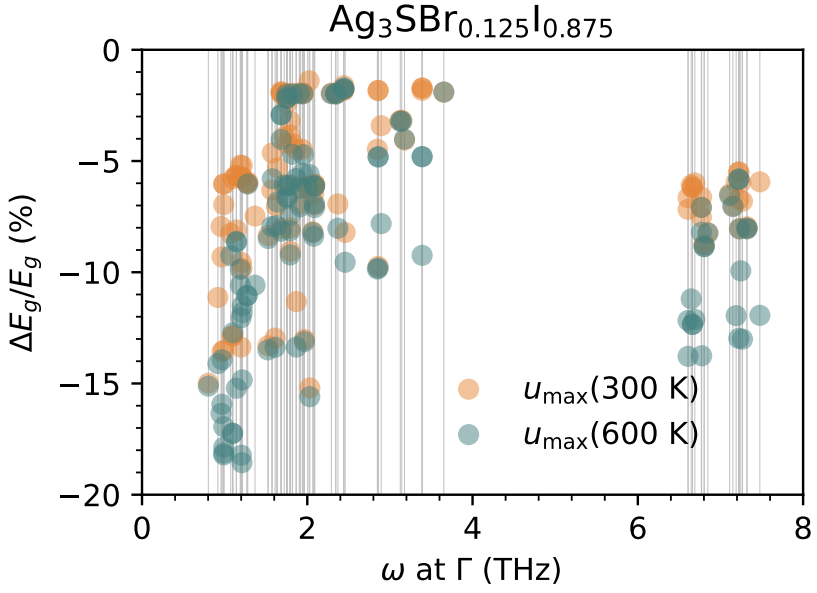
Supplementary Figure 10: Predicted relative band-gap change upon Γ-phonon mode distortions at 300 and 600 K for $Ag_3SBr_{0.5}I_{0.5}$.



Supplementary Figure 11: Predicted relative band-gap change upon Γ-phonon mode distortions at 300 and 600 K for $Ag_3SBr_{0.375}I_{0.625}$.



Supplementary Figure 12: Predicted relative band-gap change upon Γ-phonon mode distortions at 300 and 600 K for $Ag_3SBr_{0.25}I_{0.75}$.



Supplementary Figure 13: Predicted relative band-gap change upon Γ-phonon mode distortions at 300 and 600 K for $Ag_3SBr_{0.125}I_{0.875}$.

SUPPLEMENTARY DISCUSSION

To calculate the normalized cumulative occupation of vibrational states, $\chi(\omega, T)$, as function of phonon frequency, ω, and temperature, T, we employed the formula (Supplementary Fig. 7):

$$\chi(\omega, T) = \frac{\int_0^{\omega} g(z,T)\ n_{\mathrm{BE}}(z,T)\ dz}{\int_0^{\infty} g(z,T)\ n_{\mathrm{BE}}(z,T)\ dz}\ , \tag{1}$$

where g is the vibrational density of states (VDOS) and n_{BE} the Bose-Einstein distribution function expressed as:

$$n_{\mathrm{BE}}(\omega, T) = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}\ , \tag{2}$$

where $\hbar$ and k_B are the Planck and k_B Boltzmann constants, respectively.

The temperature-dependent VDOS was calculated by performing Fourier transform of the velocity autocorrelation function extracted from long molecular dynamics simulations. High-energy, unoccupied vibrational states do not contribute to the cumulative occupation function (Supplementary Fig. 7). At $T = 0$ K, and neglecting quantum nuclear effects, optical phonon modes are unoccupied, such that $\chi(\omega, 0) = 0$. As the temperature increases, low-frequency optical phonons, which are primarily responsible for the reduction of the band gap in CAP solid solutions (see main text), become progressively populated.