Strong electron-phonon coupling and quasi-1D polaron in Sb$_2$S$_3$

Yun Liu

Cavendish Laboratory, University of Cambridge,
Cambridge CB3 0HE, United Kingdom

Julia Wiktor

Department of Physics, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden

Bartomeu Monserrat

Cavendish Laboratory, University of Cambridge,
Cambridge CB3 0HE, United Kingdom and
Department of Materials Science and Metallurgy,
University of Cambridge, Cambridge CB3 0FS, United Kingdom
Abstract

Antimony sulphide (Sb$_2$S$_3$) is an Earth-abundant and non-toxic material that is under investigation for solar energy conversion applications. However, it still suffers from poor power conversion efficiency and a large open circuit voltage loss that have usually been attributed to point or interfacial defects and trap states. More recently, a self-trapped exciton has been suggested as the microscopic origin for the performance loss[1, 2]. By using first-principles methods, we demonstrate that Sb$_2$S$_3$ exhibits strong electron-phonon coupling, which results in a large renormalization of 200 meV of the absorption edge when temperature increases from 10 K to 300 K, and in a quasi-1D electron polaron that is delocalized in the ribbon direction of the crystal structure, but localized in the inter-ribbon directions. The calculated polaron formation energy of 67 meV agrees well with experimental measurements, suggesting that self-trapped excitons are likely to form with the mediation of an electron polaron. Our results demonstrate the importance of systematically investigating electron-phonon coupling and polaron formation in the antimony chalcogenide family of semiconductors for optoelectronic applications.

INTRODUCTION

Photovoltaic (PV) solar cells are one of the key technologies for realizing a decarbonized economy as the Sun is an inexhaustible and clean energy source. Mainstream solar panels have been mainly based on crystalline silicon, which offers high power conversion efficiencies (PCE) at over 25% and its cost has decreased substantially over the years[3]. While other emerging materials such as organic-inorganic hybrid perovskites and thin film technologies such as CIGS and CdTe are making rapid improvements in PCE, they still face stability, toxicity, and material scarcity issues[4]. To further increase the PCE and lower the cost of PV generated electricity, tandem solar cells show great potential as they can break the Shockley-Queisser limit of single junction solar cells[5]. The widely used silicon PV has a bandgap of around 1.1 eV and is an ideal material for the bottom cell to absorb the lower energy part of the solar spectrum. The search for top cell materials compatible with crystalline silicon is an active area of research for the scientific and engineering communities,

∗ yl398@cam.ac.uk
† bm418@cam.ac.uk
with candidates ranging from III-V semiconductors to perovskites.\[6\]

Among the many novel material candidates, the metal chalcogenide family has received a lot of attention due to their Earth-abundant and low-toxicity elements.\[7–10\] They also possess desirable band gaps and relatively benign synthesis conditions. In particular, antimony sulphide (Sb\(_2\)S\(_3\)) has a high absorption coefficient in the visible region and a band gap of 1.7 eV that is ideal for the top subcell in a Si-based tandem solar cell. Despite these promising traits, the record PCE of Sb\(_2\)S\(_3\) is only about 7.5%\[11\], far from the minimum 18% needed for an efficient top cell.\[12\] This is due to the fact that Sb\(_2\)S\(_3\) suffers from high open circuit voltage (\(V_{oc}\)) losses, even though the internal quantum efficiency is near unity and the fill factor is up to 70%. Irrespective of fabrication methods, the \(V_{oc}\) is only about 0.7 eV, half the theoretical maximum allowed by its band gap. This large \(V_{oc}\) loss has generally been ascribed to the presence of localized point defects such as sulphur vacancies or interfacial defects between Sb\(_2\)S\(_3\) and the carrier transport layers.\[13–15\] Such trap states in the band gap can act as non-radiative recombination centres to reduce photocarrier populations. Defects can also reduce the quasi-Fermi level splitting range under illumination and lead to lower \(V_{oc}\) and poor device performance.

More recently, Yang and co-workers have attributed the \(V_{oc}\) loss in Sb\(_2\)S\(_3\) to intrinsic self-trapping of carriers.\[1\] They excluded carrier trapping by extrinsic defects through a combination of a large Stokes shift of 0.6 eV, picosecond carrier trapping without saturation at high carrier densities of \(10^{20}\) cm\(^{-3}\), and the polarized nature of trap emission from Sb\(_2\)S\(_3\) single crystal. These observations instead suggest the possible formation of a hole polaron after photoexcitation, which then captures a free electron to form a self-trapped exciton (STE). A subsequent study by Grad and co-workers further expanded on the STE picture, and proposed instead that an electron polaron is formed first before hole capture.\[2\] The relative energies and the carrier lifetimes of the electron polaron and STE states were also quantified. A large Stokes shift and lattice anharmonicity were also observed in the related Sb\(_2\)Se\(_3\) films, revealing the presence of electron localization and intrinsic barrierless self-trapping.\[16\]

A prerequisite for the formation of polarons and STEs is strong coupling between the carriers and the lattice. Experimentally, the importance of electron-phonon coupling in Sb\(_2\)S\(_3\) has been studied by Chong and co-workers, who observed coherent phonon generation in pump-probe experiments, and assigned it to the \(B_{3g}\) longitudinal optical phonon mode.
| Function | a (Å)   | b (Å)   | c (Å)   | $E_g^{\text{direct}}$ | $E_g^{\text{indirect}}$ |
|----------|---------|---------|---------|-----------------------|------------------------|
| optB86b  | 11.324  | 3.865  | 11.053  | 1.241                 | 1.228                  |
| PBE      | 12.170  | 3.870  | 11.228  | 1.259                 | 1.241                  |
| PBEsol   | 11.267  | 3.829  | 10.908  | 1.307                 | 1.287                  |
| SCAN     | 11.672  | 3.847  | 11.254  | 1.382                 | 1.382                  |
| HSE06    | 12.081  | 3.802  | 11.389  | 1.745                 | 1.740                  |
| Experiment | 11.311  | 3.836  | 11.229  | 1.7                  |                        |

TABLE I. The lattice parameters and band gaps of Sb$_2$S$_3$ calculated using different DFT exchange-correlation functionals and compared with experimental values.[23]

Theoretical calculations have found the presence of large polaron radii extending over several unit cells and moderate Fröhlich coupling constants for antimony dichalcogenide systems[17]. The electronic structure and band gaps were also calculated at various levels of theory[18–20], and, separately, the phonon dispersion and anisotropic thermal expansion[21, 22]. However, a full microscopic characterization of electron-phonon coupling is still missing.

In this work, we perform a systematic first-principles study of electron-phonon coupling and polarons in Sb$_2$S$_3$. We reveal the presence of strong electron-phonon coupling, leading to a large absorption edge renormalization of 200 meV when temperature increases from 10 K to 300 K, and to the formation of a quasi-1D electron polaron with a formation energy of 67 meV. Our results support the picture in which electron polarons mediate the formation of STE in Sb$_2$S$_3$.

RESULTS AND DISCUSSIONS

A. Equilibrium properties

The orthorhombic phase of Sb$_2$S$_3$ belongs to the space group $Pbnm$ with 20 atoms per unit cell. Its crystal structure is highly anisotropic with covalently bonded 1D ribbons of Sb$_4$S$_6$ along the [010] or b direction (Figure 1(a)(b)). These ribbons are in turn weakly bonded in a zigzag fashion in the (010) plane by van der Waals interactions. Due to the presence of van der Waals interactions, we test the nonlocal vdW-DF functional optB86b[24] against some commonly used semi-local, metaGGA, and hybrid functionals[25, 28] (details in the Methods section). While most functionals are able to reproduce the b lattice parameter...
FIG. 1. (a) Sb$_2$S$_3$ crystal structure viewed from the [010] axis, with the unit cell enclosed by the black box. Brown and yellow spheres represent Sb and S atoms, respectively. One [Sb$_4$S$_6$] ribbon is encircled in the green dashed line. The intra-ribbon bonds are indicated by the solid brown-yellow lines, and the inter-ribbon van der Waals interactions by black dashed lines. (b) Sb$_2$S$_3$ crystal structure viewed from the [001] axis, with the ribbon enclosed in a green dashed line box. (c) The projected bandstructures along high symmetry lines of the Brillouin zone calculated at the optB86b level, with the orbital contributions drawn as a series of stacked circles. (d) The phonon dispersion of Sb$_2$S$_3$ along high symmetry lines of the Brillouin zone with the total phonon density of states on the right panel.

along the ribbon accurately, optB86b performs the best at simultaneously reproducing $a$ and $c$ accurately due to its better performance at capturing the van der Waals interactions in the (010) plane (see Table I).

Utilizing the relaxed structures from the optB86b functional, we then compute the orbital-projected band structure which is plotted in Figure 1(d). The valence band maximum (VBM) consists of mainly S $3p$ orbitals and the conduction band minimum (CBM) is dominated by Sb-S bonds made up of Sb $5p$ and S $3s$ orbitals. The position of the VBM and CBM are located slightly away from $\Gamma$ at $(0, 0, 0.103)$ and $(0, 0, 0.282)$, respectively. This means
that Sb$_2$S$_3$ is an indirect bandgap semiconductor, which has been reported by previous theoretical studies\cite{20}, and experimentally observed in low temperature optical measurements by Fujita and co-workers \cite{29}.

The optB86b functional suffers from the same self-interaction error as other semi-local functionals and underestimates the band gap to be around 1.24 eV (Table I). Using the hybrid functional HSE06 leads to a direct band gap of 1.75 eV that is close to the experimental value. Our results are in general agreement with previously calculated band gaps in the range 1.2-1.7 eV at different levels of theory \cite{18-20}. Due to the small difference between direct and indirect band gaps, $\Delta(E_g^{\text{direct}} - E_g^{\text{indirect}}) < 20$ meV, Sb$_2$S$_3$ is often treated as an effective direct band gap semiconductor. While hybrid functionals can more accurately reproduce the band gap, the computational cost is significantly larger than that of semilocal or vdW-DF functionals. We therefore use the optB86b functional for the electron-phonon calculations in this study and apply a HSE06-derived scissor shift to the band gaps when necessary. The computed phonon dispersion and density of states (DOS) is shown in Figure 1(d), which exhibits no imaginary modes \cite{21} indicating dynamical stability.

For polaron calculations, hybrid functionals have shown to successfully describe charge localization in a wide range of semiconductor materials \cite{30-32}. To determine the fraction of Fock exchange needed to cancel the self-interaction error, we verify the fulfillment of the Koopmans’ condition of the screened hybrid functional. This is done by calculating the occupied and unoccupied single particle energy levels related to the $+/0$ transition of an unrelaxed sulphur vacancy, which lies within the semiconductor gap of Sb$_2$S$_3$ \cite{33}. We vary the amount of exact Fock exchange while keeping the screening parameter constant at 0.2. Figure S1 shows the computed band edges and the energy levels for the $+/0$ transition of the sulphur vacancy. We note that the single-particle energy levels shown in the figure include finite-size corrections \cite{34,35}. The crossing between the levels calculated in the 0 and +1 charge of the supercell corresponds to the value of exact exchange for which the Koopmans’ condition is satisfied. This value of 0.24 is very close to the 0.25 in HSE06, which we will use as the functional for the subsequent polaron calculations.
FIG. 2. (a) Relative Helmholtz free energy as a function of the unit cell volume for temperatures between 0 and 400 K. The black dashed vertical line indicates the volume at the static DFT level, and the black squares indicate the minima of fitted free-energy curves at each given temperature with the Rose-Vinet equation of state. (b) The unit cell volume as a function of temperature as calculated by the QHA. The QHA data are also shifted by $-2.5 \text{Å}^3$ to guide the comparison with experimental volumes\[36\]. (c) Absorption coefficient at temperatures from 10K to 300K including phonon-assisted processes. A scissor operator of 0.5 eV is applied to align the static DFT bandgap to that calculated at the HSE06 level.

B. Temperature dependent structural and optical properties

The first effect we consider for the description of the finite temperature optoelectronic properties of Sb$_2$S$_3$ is the role of thermal expansion. Using the quasi-harmonic approximation (QHA)\[37\], we consider primitive cell volumes ranging from $483.5 \text{Å}^3$ to about $502 \text{Å}^3$ in 15 equidistant steps. As the unit cell of Sb$_2$S$_3$ is orthorhombic, the lattice parameters and atomic positions at each volumetric step are relaxed while keeping the volume constant. Then the Helmholtz free energies of the relaxed structures are calculated within the harmonic approximation to the lattice dynamics. Figure 2(a) depicts the Helmholtz free energy relative to the static lattice energy as a function of lattice volume for temperatures ranging from 0 to 400 K. The minimum of each fitted free-energy curve gives the quasi-harmonic volume at the corresponding temperature. The zero-point quantum motion contributes a volume increase of about $2 \text{Å}^3$, and thermal expansion increases the volume by an additional $7.5 \text{Å}^3$ in the studied temperature range.

Figure 2(b) shows the comparison between the experimental temperature dependent volume \[36\] and the QHA results. The raw DFT calculations overestimate the volume by a constant $2.5 \text{Å}^3$ from 128 K to 293 K where experimental data are available, which is mainly due to the accuracy limits of the optB86b functional. There is remarkable agreement be-
tween theory and experiment if this systematic error is corrected, revealing that thermal expansion is correctly captured by our model.

Both $E_g^{\text{direct}}$ and $E_g^{\text{indirect}}$ change by about 9 meV when considering the influence of thermal expansion from 0 K to 400 K. This change is negligible compared to the absorption edge renormalization induced by electron-phonon coupling to be discussed next. Therefore, we will ignore the effects of thermal expansion in the rest of this work.

Figure 2(c) shows the absorption spectrum of Sb$_2$S$_3$ in logarithmic scale calculated with the optB86b functional and a HSE06-derived scissor correction. The static absorption spectrum shows sharp features due to the relatively small smearing parameter of 15 meV used, which is nonetheless necessary to accurately locate the absorption onset. As the temperature increases, the optical absorption spectra are smoothed out by the continuous spectrum of allowed electronic states whose energies are renormalized by the inclusion of electron-phonon coupling effects (see Methods section for details). The absorption onset at 10 K is about 100 meV below that of the static level, indicating the importance of zero-point motion. Increasing temperature leads to a further red-shift of the absorption onset, a result that is consistent with recent experimental measurements of Bi$_2$S$_3$ in the chalcogenide family\cite{38}. The calculated absorption onset changes by around 200 meV from 10 K to 300 K, somewhat larger than that of 159 meV reported for Bi$_2$S$_3$, but the difference likely arises from the mass difference between Bi and Sb. Absorption onset redshifts of about 100 meV have been observed in other conventional III-V or van der Waals semiconductors (see Table II).

The large redshift in the temperature dependent absorption onset shows that Sb$_2$S$_3$ exhibits large electron-phonon coupling. Such strong coupling between electrons and phonons provides the necessary conditions for the possible generation of small localized polarons and STEs, which we discuss next.

C. Quasi-1D electron polaron

Strong coupling between excitons and phonons can lead to the localization of the carrier due to local deformations of the lattice. In 3D, these deformations generate a potential barrier acting as a trap, and free excitons need to pass this barrier to self-trap\cite{42}. By contrast, in 1D systems there is no energy barrier to self-trapping if the lattice vibrations are treated classically, and free and self-trapped excitons can co-exist\cite{43, 44}.
| Material | $\Delta E_g$ (meV) | References |
|----------|------------------|------------|
| Sb$_2$S$_3$ | 200              | This study |
| Bi$_2$S$_3$ | 159              | [38]       |
| GaAs     | 96               | [39]       |
| GaSb     | 85               | [39]       |
| MoS$_2$  | 95               | [40]       |
| WSe$_2$  | 66               | [41]       |

TABLE II. The change in bandgap for selected semiconductors in the temperature range from 10 to 300K.

FIG. 3. (a) The charge density isosurface representation of the quasi-1D shape of the self-trapped electron in Sb$_2$S$_3$ as viewed along the (a) [010] and (c) [001] directions. The charge density of the hole states is delocalized and does not show signs of polaron formation, as viewed along the (b) [010] and (d) [001] directions. The charge density value at the isosurface is $1 \times 10^{-4}$ eÅ$^{-3}$.

The formation of a STE can either occur directly after photoexcitation or via a 2-step process where the first step is the formation of either or both an electron or hole polaron[45]. The electron or hole polaron can then capture a hole or electron, respectively, to form a STE. In Sb$_2$S$_3$, the literature seems to agree that the STE forms in a 2-step process, as there is a saturation in the carrier decay kinetics as a function of photoexcited carrier density[1, 46], as well as the detection of two trap-like states below the CBM[2]. However, it is less clear whether it is electron or hole polarons that first form after photoexcitation. One argument is that the hole polaron will form first due to the smaller hole mobility and larger hole effective masses[47, 48]. By contrast, time-resolved two-photon photoemission reveals the presence...
of 2 distinct trap states at 60 meV and 440 meV below the CBM with lifetimes of 27 ps and 63 ps, respectively. The self-trapped electron is assigned to the shallow trap and the STE to the deeper trap.

To resolve some of these controversies, we investigate the possible formation of both electron and hole polarons. To find the polaronic geometry, we apply the bond distortion method to various Sb-S bonds to break the symmetry of the crystal structure\cite{49}, which has shown to give faster convergence by mimicking the experimentally observed polaronic distortions. An electron is then added/removed from the supercell and the atomic positions are relaxed (see details in Methods section).

Figure 3(a) shows the charge density of the added electron mainly localized on the Sb atoms located on the edges of a [Sb$_4$S$_6$] ribbon, after structural relaxation. The charge density can be seen forming a uniform chain along the [010] or ribbon direction as shown in Figure 3(c). The geometry of the polaron is consistent with the highly anisotropic quasi-1D crystal structure of the system. On the other hand, the charge density of the hole state is delocalized over the entire [Sb$_4$S$_6$] ribbon, and over into neighbouring ribbons, showing no sign of localization, as depicted in Figures 3(b)(d). Given these observations, we postulate that the hole polaron does not form in Sb$_2$S$_3$, and is not likely to be a pathway for the eventual formation of the STE. We also estimate the binding energy of the electron polaron as 67 meV. We note that this value is very close to energy of the shallow trap at 60 meV below the CBM measured using time-resolved two-photon photoemission.

To assess the effect of thermal disorder on the electron localization, we perform molecular dynamics (MD) simulations of the electron polaron [Movie in Supporting Information]. The degree of the excess charge localization is quantified using the Inverse Participation Ratio (IPR)

\[
\text{IPR} = \frac{\sum_i |\Phi_i|^4}{(\sum_i |\Phi_i|^2)^2}
\]

where $\Phi_i$ is the electronic wavefunction. In this definition of IPR, a localized state has a value of 1 and it tends towards $\frac{1}{V}$ for complete delocalization where $V$ is the total volume of the system. Figure 4a shows the IPR of the excess electron for the duration of the MD simulation. The system undergoes cycles of localization and delocalization, with the polaron hopping between different chains. For example, the polaron is delocalized across the entire system.
FIG. 4. (a) The Inverse Participation Ratio (IPR) of the wavefunction of the excess electron during the MD simulation. The blue dots indicates the positions where we visualize the charge densities, representing a series of delocalization, followed by localization and then delocalization again. (b)-(d) The charge density isosurface of the electron polaron as viewed along the [010] direction at $t = 2.45$ ps, $t = 2.675$ ps and $t = 2.975$ ps. The charge density value at the isosurface is $1 \times 10^{-4} \, e\, \text{Å}^{-3}$.

with a high charge density on a $[\text{Sb}_4\text{S}_6]$ chain at the top of the supercell at 2.45 ps (Figure 4b), before localizing mainly along two $[\text{Sb}_4\text{S}_6]$ chains that are slightly translated from the original high charge density areas at 2.675 ps (Figure 4c). The system then delocalizes slightly again along the centre of the $[\text{Sb}_4\text{S}_6]$ chains in the supercell (Figure 4d). The degeneracy of the many 1D channels in the electron polaron is broken with thermal disorder as seen in the MD simulation. We would like to point out that the multiple hoppings mediated by a series of localized and delocalized states of the carrier has been observed in 1D organic semiconductors[50], with the transport mechanism explained successfully using the transient localization theory as somewhere in between of the band and hopping regime[17, 51].
CONCLUSION

We studied electron-phonon coupling in the quasi-1D semiconductor Sb$_2$S$_3$. We first showed that the optB86b nonlocal vdw-DF functional is the best choice for reproducing the experimental lattice parameters. The quasi-harmonic approximation is capable of reproducing the thermal expansion coefficient and volumes agree well with experiments. We showed that the absorption edge redshifts going from 10 K to 300 K by around 200 meV, higher than the corresponding shift observed in most conventional and van der Waals semiconductors. This shows that there is significant electron-phonon coupling in the system. In the presence of excess electrons, a quasi-1D electron polaron is formed with a predicted binding energy of 67 meV, which agrees well with experimental measurements. This provides evidence to support that the formation of STE occurs first via the formation of an electron polaron. Thermal disorder further localizes the excess charge onto a few chains and it hops to other chains through first delocalizing over the entire system. The presence of electron-phonon coupling and formation of a 1D polaron play an important role for the optoelectronic properties, and might place a fundamental limit on the open circuit voltage of photovoltaic devices and consequently on the maximum efficiency of Sb$_2$S$_3$ solar cells.

METHODS

All DFT calculations are performed using the Vienna Ab initio Simulation Package (VASP, v5.4)\textsuperscript{52, 53}. The core-valence interaction is described using the projector-augmented wave (PAW) method\textsuperscript{54}, with 5 valence electrons for Sb ($5s^25p^3$) and 6 valence electrons for S ($3s^23p^4$). The electronic wave functions are expanded in a plane wave basis with an energy cutoff of 400 eV, the Brillouin zone is sampled with a $12 \times 4 \times 12$ Γ-centered Monkhorst-Pack\textsuperscript{55} $k$-point grid, and commensurate grids for the supercells. The atoms are relaxed until the Hellman-Feynman force converges below 0.001 eVÅ$^{-1}$, and the volume until all components of the stress tensor are below 10$^{-2}$ GPa.

All phonon dispersions are computed using the finite displacement method with a $2 \times 6 \times 2$ supercell containing 320 atoms (22.647Å $\times$ 23.189Å $\times$ 22.106Å) as implemented in the Phonopy package\textsuperscript{56}. For phonon dispersions, a non-analytical term is added to the dynamical matrix to treat the long range interaction arising from the macroscopic electric field induced by the
polarization of collective ionic motions near $\Gamma[57]$. 

To include the effects of electron-phonon interactions to optical absorption at a given temperature $T$, we evaluate the imaginary part of the frequency-dependent dielectric function $\varepsilon_2(\omega, T)$ within the independent particle approximation using the Williams-Lax theory:

$$\varepsilon_2(\omega, T) = \frac{1}{Z} \sum_s \langle \Phi_s(u)|\varepsilon_2(\omega, T)|\Phi_s(u) \rangle e^{-E_s/k_B T},$$

(2)

where $\Phi_s$ is the vibrational wave function in state $s$ and with energy $E_s$, evaluated within the harmonic approximation, and $Z = \sum_s e^{-E_s/k_B T}$ is the partition function in which $k_B$ is Boltzmann’s constant. For these calculations, we re-compute the phonon frequencies and eigenvectors using non-diagonal supercells[58], and then use them as a starting point to evaluate Equation (2) with Monte Carlo integration accelerated by thermal lines[59, 60].

From the finite temperature dielectric function, the absorption coefficient is given by $\alpha(\omega) = \frac{\omega}{cn(\omega)}\varepsilon_2(\omega)$, where $c$ is the speed of light in vacuum, $\varepsilon_2(\omega)$ is the imaginary part of the dielectric function, and $n(\omega)$ is the real part of the complex refractive index. $n^2(\omega) = \frac{1}{2}(\varepsilon_1 + \sqrt{\varepsilon_2^2 + \varepsilon_1^2})$ where $\varepsilon_1(\omega)$ being the real part of the dielectric function. $\varepsilon_1(\omega)$ is obtained from $\varepsilon_2(\omega)$ through the Kramers-Kronig relation. Convergence tests show that a $2 \times 6 \times 2$ supercell and a $2 \times 2 \times 2$ electronic $k$-grid lead to accurate results.

For the fulfillment of the Koopmans’ condition, the corrections to the unoccupied Kohn-Sham eigenvalues of the defect-induced single particle levels are calculated as[61]

$$\varepsilon_{KS}^{\text{corr}} = -\frac{2}{q} E_{\text{corr}}$$

(3)

where $q$ is the charge of the defect, and $E_{\text{corr}}$ is finite-size electrostatic correction. $E_{\text{corr}}$ is computed using sxdefectalign[34] with an anisotropic screening where the diagonal terms of the high-frequency dielectric tensor $\varepsilon_{xx} = 11$, $\varepsilon_{yy} = 8$, $\varepsilon_{zz} = 12$ are used[18].

For polaron calculations, we use a $2 \times 4 \times 2$ supercell to minimize spurious interactions between periodic images, and sample only the $\Gamma$-point. After the addition or removal of an electron from the supercell, structural relaxation is performed using spin-polarized calculations whereby the supercell lattice parameters are fixed and the atoms allowed to move, with the same force convergence criterion of $0.001 \text{eV\AA}^{-1}$. The binding energy of the electron polaron can be estimated using the following formula for defect formation energy
where $E_{q[\text{polaron}]}$ is the total energy of the distorted supercell of the electron polaronic state, $E_{[\text{pristine}]}$ is the total energy for the perfect crystal using an equivalent supercell, with $q$ denoting the excess of charge of an electron ($q = -1$), $E_{\text{CBM}}$ is the position of the CBM. The diagonal components of the static dielectric tensor are used with $\varepsilon_{xx} = 94$, $\varepsilon_{yy} = 13$, $\varepsilon_{zz} = 99$.

The molecular dynamics (MD) simulation of the extra electron was carried out using the HSE06 hybrid functional within the CP2K code. We used DZVP-MOLOPT basis sets and the plane wave cutoff energy of 400 Ry. Core-valence interactions were described by Goedecker-Teter-Hutter pseudopotentials. The simulation was performed with the auxiliary density matrix method (ADMM). The MD run was carried out in the NVT ensemble in a 320-atom supercell. The volume was set to the equilibrium volume calculated within HSE06 using VASP. The temperature was set to 300 K and controlled by a Nosé-Hoover thermostat. We employed a time step of 5 fs and carried out the run for 4 ps.

Crystal structures and isosurfaces are visualized using VESTA and graphs are plotted by sumo and custom scripts.

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