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Ionic current and polarization effect in TlBr

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Thallium bromide (TlBr) is an ionic semiconductor that has shown great capacity for accurate radiation detection. Its application to this end, however, has been hampered by degradation of performance over time, in a process called polarization. This effect has been traditionally assigned to a build-up of ions at the electrodes, which would counteract an applied electrical bias field. Here, we estimate the ionic mobility in TlBr and its possible association with the polarization effect using parameter-free quantum simulations. Our results indicate that in samples with up to moderate levels of impurities, ions cannot traverse distances large enough to generate zones of accumulation and depletion in the crystal, suggesting different causes for the polarization effect.

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In recent years, thallium bromide has emerged as one of the most promising materials for sensitive room temperature γ- and x-radiation detection, achieving resolution as fine as 1% at 662 keV or better.[1,2] The high-performance stems from the material's favorable properties, namely, a moderate band gap (2.7 eV), very long carrier drift length (lifetime up to 10^{-4} s), high room-temperature resistivity (around 10^{11} $\Omega\,\mathrm{cm}^{-1}$),[3] and high average atomic number.[4] However, its widespread adoption for radiation detection applications—such as medical and space imaging or port monitoring for national security—has been prevented due to invariable performance degradation after operation times that vary from hours to several weeks.[5] This effect, termed polarization, has been assumed to be associated with the accumulation of oppositely charged ions (Tl^+ and Br^-) at the electrical contacts of the device, from migration of the ions in opposite directions via vacancy hopping under an applied bias field. The resulting charge build up would counter the applied electric field and impair the collection of photoinduced carriers, degrading detection performance. Different remedies have been attempted to prevent this degradation, including using thallium contacts,[6] cooling the detectors,[7] employing various surface treatments,[8] and others. No technique has yet been able to solve the degradation problem indefinitely.

In this Rapid Communication, we describe a quantitative theoretical estimation of ionic migration in TlBr to compare against the observed degradation times. Drift ionic mobility can be evaluated by the Einstein-Smoluchowski relation:

$$\mu = \frac{qD}{kT} \tag{1}$$

with the diffusivity given by the expression[9]

$$D = f\nu_0 a_0^2 \sum_{i=\mathrm{Tl,Br}} \left\{ \exp\left[-\left(\Delta G_m^i + \Delta G_f^{\mathrm{vacs}}\right)/kT\right] + \tilde{n}_{\mathrm{vac},i}^{\mathrm{excess}} \exp\left(-\Delta G_m^i/kT\right) \right\} \tag{2}$$

for the vacancy-hop mechanism, where q is the charge of the mobile species, k is the Boltzmann constant, f is a factor dependent on the lattice, a_0 is the jump distance of an ion, ν_0 is the frequency of vibration of the ion in the jump direction (attempt frequency), ΔG_m is the migration free energy barrier, and $\Delta G_f^{\mathrm{vacs}}$ is the average Gibbs free energy of formation of both types of vacancies for a given value of the Fermi level. For TlBr ($Pm\bar{3}m$ structure), the ions move in $\langle 100\rangle$ directions on equivalent sites forming a simple cubic lattice, for which $f = 0.655$ and a_0 equals the lattice constant. The term $\tilde{n}_{\mathrm{vac},i}^{\mathrm{excess}}$ is a given concentration of vacancies per unit cell, i.e. the concentration per cm^3 divided by a_0^3. It accounts for the possibility of an extrinsic concentration of vacancies, which may form to keep charge neutrality in the presence of charged impurities, for example.[10]

In order to theoretically estimate ionic current in TlBr, all quantities in Eqs. (1) and (2) can be obtained from parameter-free quantum mechanical simulations. We use density functional theory[11] with the generalized gradient approximation for the exchange-correlation as developed by Perdew, Burke, and Erzenhof (PBE).[12] We performed tests using more accurate HSE06 hybrid functional[13,14] in smaller cells and verified the accuracy of PBE for the analysis presented here.[10] The projector augmented-wave method,[15] as implemented in the VASP code,[16–18] is used to treat core electrons. A plane-wave basis with an energy cutoff of 320 eV is used. For Brillouin zone sampling, we use the tetrahedron method with a Monkhorst-Pack mesh of 5 × 5 × 5 k-points for a 4 × 4 × 4 supercell (128 atoms). Atomic coordinates were relaxed until all residual forces were below 0.01 eV Å^{-1}. For pristine TlBr, we obtain a direct band gap of 1.98 eV and a lattice parameter of 4.06 Å, compared to experimental values[19] of 3.01 eV (direct gap) and 3.97 Å.[20]

The formation energies of defects are given by[21]

$$\Delta E_f = E_d - \left(E_p - \sum_i n_i \mu_i\right) + q(\mu_e + E_{\mathrm{VBM}}), \tag{3}$$

where E_d and E_p are the total energies of the defective and the pristine supercells, respectively, n_i is the number of atoms of element i removed from the supercell and added to a reservoir whose chemical potential is μ_i, and q is the charge exchanged with a reservoir at an electron chemical potential μ_e, which we reference to the energy of the valence band maximum, E_{VBM}. Spurious periodic electrostatic interactions for supercells with charged defects were corrected with the Makov-Payne scheme,[22] with $\varepsilon = 5.7\varepsilon_0$.[23] The chemical potentials in the stoichiometric regime are given by $\mu_{\mathrm{Tl(Br)}} = \mu^0_{\mathrm{Tl(Br)}} + \Delta H_{f,\mathrm{TlBr}}/2$, where $\Delta H_{f,\mathrm{TlBr}} = \mu_{\mathrm{TlBr}} - \mu^0_{\mathrm{Tl}} - \mu^0_{\mathrm{Br}}$.[24,25] The superscript 0 denotes the bulk phase:

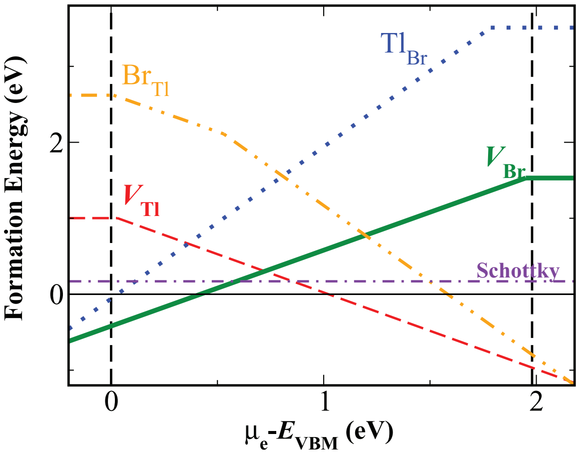

FIG. 1. (Color online) Formation energies of intrinsic defects in TlBr: E$_f$ of positively charged Br vacancies coincides with that of negatively charged Tl vacancies near the middle of the band-gap, pinning the Fermi level. Neutrally charged complexes of vacancies (Schottky pairs), Tl and Br antisites are also indicated. The vertical dashed lines indicate the positions of the calculated band edges.

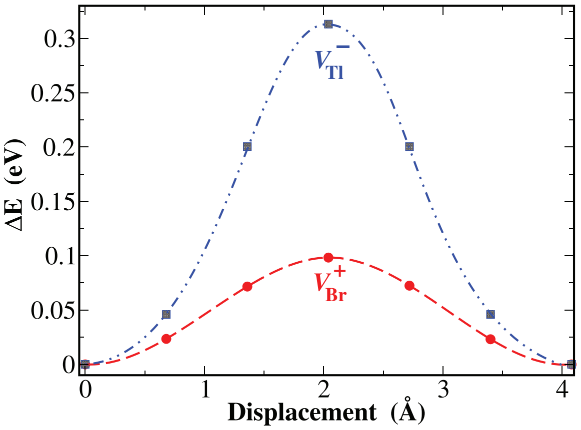

FIG. 2. (Color online) Calculated migration barriers of charged Tl (blue squares) and Br (red circles) vacancies obtained using the nudged elastic band method. The lines are guides to the eye.

$\mu^0_{\rm Tl} = -2.36$ eV (hexagonal structure) and $\mu^0_{\rm Br} = -1.62$ eV (Br$_2$ gas). The equilibrium concentration of each defect is then given by $c = c_0 \exp(-E_f/k_B T)$.

In Fig. 1, we show the calculated formation energies for vacancies and antisite defects in TlBr as a function of electron chemical potential. The slopes of the curves indicate the charge state of the defect and kinks mark transition levels. The vertical dashed lines indicate the positions of the calculated band edges. Because of the pinning of the Fermi level near the middle of the band gap, indicated by the crossing of the formation energy curves of $V_{\rm Tl}^-$ and $V_{\rm Br}^+$, as well as the low formation energies of these defects, TlBr is driven to generate extra charged vacancies in response to any excess charge introduced by impurities.[9,10,26,27] Thus inclusion of the $\tilde{n}^{\rm excess}_{{\rm vac},i}$ term in Eq. (2) is of fundamental importance to estimate the relationship between concentration of impurities and the ionic current. From Eq. (3), we obtain $\Delta E_f^{\rm vacs} = (\Delta E_f^{V_{\rm Br}^+} + \Delta E_f^{V_{\rm Tl}^-})/2$ to be plugged into Eq. (2). We found $\Delta E_f^{\rm vacs} = 0.3$ eV using PBE with a $4 \times 4 \times 4$ supercell. The calculated values are quite lower than experimental estimates of $2\Delta G_f^{\rm vacs} = 0.91$ eV.[27] As a result, simulations predict a larger concentration of intrinsic vacancies in TlBr and therefore larger ionic currents, as we will discuss in the sequence.

Other terms in Eq. (2) can be estimated from the potential energy surface, which we sample using the nudged elastic band method with the climbing image implementation.[28] The height of the migration barrier in Fig. 2 give ΔG_m. The attempt frequency ν_0 in Eq. (2) can be obtained within harmonic transition-state theory via the Vineyard equation,[29] which involves the ratio of the product of the system's stable vibrational modes in the ground versus transition states. If we make the reasonable assumption that only the degree of freedom of the hopping atom in the direction of the vacancy hop is important, ν_0 can be extracted from the curvature at the bottom of the migration barrier within the harmonic approximation. From the data in Fig. 2, we obtained ΔG_m of 0.31 eV and 0.10 eV for the migration barriers of Tl$^+$ ($V_{\rm Tl}^-$) and Br$^-$ ($V_{\rm Br}^+$), respectively, and ν_0 of 0.43 THz and 0.38 THz for Tl$^+$ and Br$^-$, respectively. These values of ν_0 are similar to the short-wavelength transverse acoustic phonon frequency in the X direction (the hop direction).

To properly estimate the diffusivities with Eq. (2), we also must consider that vacancies can bind with oppositely charged species and become less mobile. To account for such binding, we must replace $\Delta E_m (= \Delta G_m + T\Delta S_m)$ with an effective migration barrier given by $\Delta E_{m,{\rm eff}} = \Delta E_m + 0.5\Delta E_{\rm bind}$,[9] where the binding energy of defect complexes is given by[30]

$$\Delta E_{\rm bind} = \sum_i E_{d,i} - E_{\rm complex}. \tag{4}$$

Here, $E_{\rm complex}$ is the formation energy of the defect complex, $E_{d,i}$ are the formation energies of each individual defect that comprise the complex, and $\Delta E_{\rm bind} > 0$ denotes binding, following the convention adopted in Ref. 31. For TlBr, we calculate the binding energy for Schottky pairs ($V_{\rm Tl}^- + V_{\rm Br}^+$) as 0.44 eV, resulting in effective migration barriers of 0.53 and 0.32 eV for Tl$^+$ and Br$^-$, respectively, for bound vacancies. These effective barriers also have been estimated experimentally as 0.51 and 0.28 eV for Tl$^+$ and Br$^-$, respectively, by Bishop *et al.*[27] and as 0.56 and 0.25 eV, respectively, by Samara.[26,33]

To asses whether the inclusion of the binding term in the evaluation of the theoretical migration barriers of Tl$^+$ and Br$^-$ ions is justified, we need to estimate the relative proportion of bound to free vacancies in the crystal. An estimate can be made by evaluating[31,34]

$$p = \frac{n_{\rm pair}}{n_{\rm free}} = z \exp\left(\frac{\Delta G_{\rm bind} - \Delta G_f^{\rm vacs}}{k_B T}\right), \tag{5}$$

where z is the coordination number of vacancy pairs (i.e., the number of ways of forming the pair at a particular site) and $\Delta G_{\rm bind} = \Delta E_{\rm bind} - \Delta S_{\rm bind} T$, with $\Delta S_{\rm bind}$ the entropy change due to the association of the vacancies. Considering bound pairs of vacancies occupying nearest-neighbor sites, for TlBr we have $z = 8$. The entropies of formation and association of the pairs can be estimated using the expressions[31]

$$\Delta S_f = (10.8 E_{\rm bind} - 2.56)\, k_B \tag{6}$$

and

$$\Delta S_{\text{bind}} = \left[\ln([V_c]) + \frac{4L}{N k_B T_m} \right] 2k_B, \qquad (7)$$

where $[V_c]$ is the critical mole fraction of vacancies at melting (8.5×10^{-4} for TlCl[31]), T_m is the melting temperature (732 K for TlBr[31]), L is the heat of fusion (16.3 kJ/mol for TlBr[31]), and N is Avogadro's constant. Equation (6) is empirical and was obtained by fitting several experimental results, whereas Eq. (7) comes from assuming that melting occurs when the concentration of thermally generated vacancies reaches a critical value. Using these expressions with the formation energy from Ref. 27 and an association energy of 0.44 eV from our calculations, we get that at room temperature, there are about 20 times more vacancies bound in neutrally charged pairs than isolated ones. Using instead the calculated formation energy for Schottky pairs, we get that at room temperature, the number of vacancy pairs is four orders of magnitude higher than that of free vacancies in the crystal. We note that even disregarding the entropy terms approximated by Eqs. (6) and (7), these conclusions are qualitatively maintained. Moreover, our results show that oppositely charged vacancies are not only bound on nearest-neighbor sites, but also at least on second nearest-neighbor sites; therefore the effective value of z in Eq. (5) is underestimated and should be at least as high as 24. Thus the values of p given above are lower estimates. Consequently, we conclude that most vacancies will be paired in neutral complexes rather than being isolated in TlBr at room temperature, explaining the good agreement between the experimental and theoretical results for the migration barriers of Tl^+ and Br^- ions.

In Fig. 3, we plot the ionic mobilities $\times$ $T(K)$ versus T^{-1} for different concentrations of extrinsic vacancies using Eqs. (1) and (2). These data are based on considering complete association of vacancies into neutral pairs, using the binding energy between V_{Tl} and V_{Br} as a common value for binding between vacancies and any charged defect, which was shown to be reasonably accurate for several impurities in Ref 10. Excess vacancy concentrations must be higher than 10^{17} cm^{-3} to affect ionic mobilities at room temperature. Using the data from Ref. 27, this threshold changes to 10^{15} cm^{-3}, because of the smaller concentration of vacancies due to the higher formation energy relative to the theoretical estimate. Overall, however, the qualitative behavior is similar in either case. We also show the extrinsic concentrations needed to affect the mobilities at −20 °C, a temperature at which the polarization effect significantly slows down.[7] We further show the required extrinsic concentrations of V_{Tl} to make Tl^+ ions more mobile than Br^- (assuming intrinsic concentration of V_{Br}): 10^{21} cm^{-3} V_{Tl} with completely associated vacancies, a concentration so high that the crystal would likely become unstable and melt.[31] Using the experimental data, we find that 10^{19} cm^{-3} extrinsic V_{Tl} would be needed to change the majority carriers to Tl^+. At such high concentrations of defects, many of the approximations we used become less reliable,[34] therefore these results involve larger errors than the ones with concentrations below 10^{19} cm^{-3}.

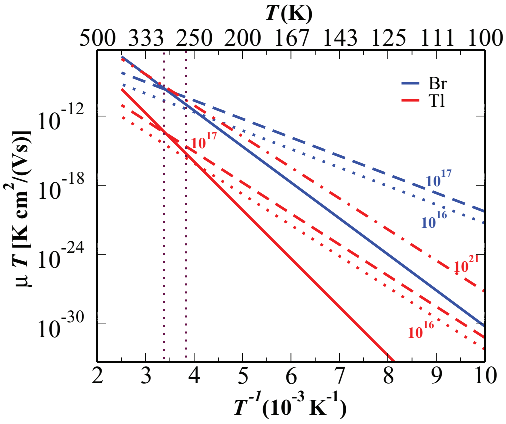

FIG. 3. (Color online) Ionic mobility, μ, as a function of T^{-1} for Br^- (blue) and Tl^+ (red) ions in TlBr. The solid lines are plotted for the case of intrinsic concentrations of vacancies, while the dotted and dashed lines correspond to cases with additional extrinsic concentrations of vacancies as indicated next to each line (in cm^{-3}). These results were obtained using our calculated parameters, assuming that all vacancies are associated in pairs with oppositely charged defects. The binding energy assumed was the same as that of Schottky pairs. The dash-dotted curves correspond to the required extrinsic concentration of Tl vacancies so that Tl^+ ions become the majority carriers at room temperature, given intrinsic concentrations of V_{Br}^+. The vertical dotted lines indicate room temperature and −20°C.

In Table I, we show the calculated time it would take a Br^- ion to traverse a distance of 1 mm in the crystal under an applied bias of 1000 V cm^{-1}, for different concentrations of extrinsic vacancies. Taking the experimental parameters and considering reasonably high extrinsic concentrations of V_{Br}^+, up to 10^{17} cm^{-3}, the times are in order of years, which is inconsistent with the longest observed stable operation of a TlBr radiation detector at room temperature—on the order of a few months.[1,2] Thus, for a time-dependent polarization effect to be caused by drift of Br^- ions, the extrinsic concentrations of vacancies must be significantly higher than 10^{17} cm^{-3}. Otherwise, our calculations show that the experimental estimate of the migration barrier for Br^- would have to be wrong by nearly 300% to accommodate the hypothesis of detector degradation within a few hours due to intrinsic charge gradients within the crystal. For example, if ΔE_m^{Br} were only 0.1 eV—a discrepancy of 70% from the experimental estimate—it would take about 8.5 hours for a Br^- ion to traverse a distance of 1 mm within an intrinsic TlBr crystal. If ΔE_m^{Br} were 0.25 eV, a discrepancy of 21% from the experimental estimate, a Br^- ion would take about 75 days to move 1 mm in an impurity free crystal. In Ref. 10, we calculated the effect of codoping TlBr with Se and Pb, showing that in this case there is occurrence of

TABLE I. Time in years for the more mobile Br^- ions to drift a distance of 1 mm at room temperature under an applied bias of 1000 V/cm in TlBr crystals with different concentrations of extrinsic vacancies at room temperature. Times are shown using both the experimental and theoretical estimates for the relevant parameters.

Extrinsic concentration (cm^{-3})	0	10^{16}	10^{17}	10^{18}	10^{19}
Experiment. parameters[a]	270	9.3	0.96	0.10	0.01
Associated vacancies	2.7	2.5	1.5	0.32	0.036

[a] ΔG_m and ΔG_f from Ref. 27.

defect complexes involving both dopants and both types of vacancies that bind more than three times more strongly than the Schottky pairs. Reproducing the analysis above for the material doped in this way, we find that migration times for the vacancies, even with extrinsic concentrations of vacancies of 10^{19} cm^{-3}, would be of the order of 10^6 years. This indicates that such a treatment would be a very effective alternative to ultrapurification of TlBr. This hints at either high concentrations of extrinsic vacancies in TlBr, meaning high impurity levels, or different causes for the degradation of the energy resolution of these radiation detectors than that commonly accepted. This important conclusion has been overlooked in current efforts to construct stable and accurate TlBr radiation detectors.

In summary, we have estimated the diffusivities of intrinsic ions in TlBr using DFT with the PBE and HSE06 exchange-correlation functionals. By accounting of the binding of oppositely charged vacancies into pairs, very good agreement between the theoretical effective migration barriers and the experimental measurements is obtained. We estimate that there are more bound than free vacancies in TlBr at room temperature. This explains the agreement we found between the theoretical and experimental migration barriers and indicates that the possibility of binding of vacancies, although frequently overlooked, should be considered in simulations of systems where ionic current is modelled. Using both the experimental and our theoretical data, we estimated the time required for the faster species, Br$^-$ ions, to traverse a distance of 1 mm in the crystal under 1000 V cm^{-1} bias at room temperature. We showed that this migration takes too long to account for the observed degradation of TlBr detectors in less than about 1 year, unless the samples have very large levels of contamination (at least around 10^{17} cm^{-3}), which is not consistent with measured impurity concentrations. For a TlBr crystal codoped with Pb and Se ions, as discussed in Ref. 10, these migration times are extremely high, indicating an alternative to purification. Our results strongly indicate that the origin of the loss of resolution and sensitivity over time of TlBr radiation detectors is not exclusively the accumulation of Br$^-$/Tl$^+$ at the contacts.

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