Decisive Roles of Intersite Coulomb Interactions in Charge Ordered Systems

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Using ab initio approaches for extended Hubbard interactions coupled to phonons, we reveal that the intersite Coulomb interaction plays decisive roles in determining various distinctive phases of the paradigmatic charge ordered materials of Ba$_{1-x}$K$_x$AO$_3$ ($A = \text{Bi and Sb}$). We demonstrated that all their salient doping dependent experiment features such as breathing instabilities, anomalous phonon dispersions, and transition between charge-density wave and superconducting states can be accounted very well if self-consistently obtained nearest neighbor Hubbard interaction are included, thus establishing a minimal criterion for reliable descriptions of spontaneous charge orders in solids.

Since Verwey found the metal-to-insulator transition (MIT) in magnetite (Fe$_3$O$_4$) owing to long-range order of alternating Fe$^{3+}$ and Fe$^{4+}$ ions [1], the charge ordered state has been one of the central issues in condensed matter physics. It often occurs near MITs, superconducting (SC), or charge density wave (CDW) states [2–9]. These local charge ordering (CO) can lead to colossal magnetoresistance, ferroelectricity or multiferroicity [10, 11]. In addition, the CO in high-temperature cuprate superconductors has also been studied intensively to understand its roles as a leading competitor of SC state [4–7].

Charge ordered materials host atoms with disparate charging states that are closely placed, invoking the strong Coulomb interactions and distorting lattices to relieve their energetic cost [12]. Hence, theories and computations for the systems should treat the interaction as well as its coupling to lattices on an equal footing. Typical approaches based on density functional theory with the local density approximation (DFT-LDA) [13] or generalized gradient approximation (GGA) [14] fail to describe their properties [15, 16]. The addition of on-site Hubbard interaction ($U$) within DFT (DFT+U) [17, 18] captures a correct CO state when the intersite interaction is well screened [15]. Except few cases, however, it is insufficient in obtaining the proper ground states [19–21]. Therefore, advanced methods beyond the local corrections are needed to figure out the role of the interactions in COs and their evolution with doping.

Perovskite BaBiO$_3$ (BBO) and BaSbO$_3$ (BSO) are prototypical CO materials that are not well understood by DFT-GGA and DFT+U [22–34]. They show CDW states characterized by breathing distortion of oxygen octahedra with the charge disproportionations of Bi ions [22–24]. The CDW is suppressed by substituting Ba with K and SC phase occurs at relatively higher transition temperature ($T_c$) [8, 9]. A few recent studies based on the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional and GW approximation (GWA) can capture the insulating ground state of BBO and obtain enhanced electron-phonon ($e$-$p$) interactions, providing a clue to understanding the observed $T_c$ [31–35]. However, realistic full phonon spectra to understand the transition between SC and CDW states for experimentally accessible doping levels are hardly available due to demanding computational resources and computed frequency is usually overestimated for strongly coupled phonons [26, 33, 34].

On the other hand, recent developments on self-consistent evaluations of $U$ [36, 37] and intersite Hubbard interactions ($V$) [38, 39] within DFT (DFT+U+$V$) [40] successfully describe various properties of solids [38–48]. Owing to their low computational cost comparable to DFT-LDA and improved accuracy to GWA [38, 46], the new method provides an opportunity to study the correlated solids in large scale structures and full phase space of interests. Motivated by these developments as well as the works on BBO and BSO, we have carried out ab initio study to explore the role of the interactions for interplay between their electronic and structural properties.

In this work, we theoretically demonstrate that the evolution of charge ordered states in bismuthates and antimonates with potassium doping is essentially controlled by the doping-dependent non-local Coulomb interaction. Our new parameter-free ab initio method for extended Hubbard interactions [38, 46] can compute electronic energy bands as well as full phonon dispersions of Ba$_{1-x}$K$_x$AO$_3$ ($A = \text{Bi and Sb}$) for the whole phase space with structural phase transitions, agreeing well with all the key measurements only when intersite Coulomb interactions are included. Our establishments implies that the explicit treatment of the non-local interactions is critical for the description of the intertwined charge and lattice degrees of freedom in charge ordered materials.

Our DFT+U+$V$ method uses the total energy functional of $E_{\text{tot}} = E_{\text{DFT}} + E_{\text{Hub}}$ that can be decomposed into (semi)local density functional of $E_{\text{DFT}}$ and Hubbard functional with double counting corrections [40], $E_{\text{Hub}} = \frac{1}{2} \sum_{I} U_{I} \sum_{m,m',\sigma} (\delta_{m,m'} - \delta_{m,m'}) n_{I,m}^{\sigma} n_{I,m'}^{\sigma}$ $- \frac{1}{2} \sum_{\lbrace I,J \rbrace} V_{I,J} \sum_{m,m',\sigma} n_{I,m}^{\sigma} n_{J,m'}^{\sigma}$, where the generalized occupation matrix is $n_{m}^{I,\sigma} = \sum_{k} f_{k,m} \phi_{m \sigma}^{I}$, $\langle \phi_{m \sigma}^{I} | \phi_{m' \sigma}^{J} \rangle$, the Fermi-Dirac function of Kohn-Sham orbital of $\psi_{k,m}^{\sigma}$ of the rth band with spin $\sigma$ at momentum k, and $\phi_{m}^{I}$ the localized orbitals with angular quantum number $m$. Here, $I$ and $J$ are abbreviated indexes...
for atomic positions and principal and azimuthal quantum numbers together and \( \{I, J\} \) denotes a pair of atoms within the nearest neighboring distances. We obtain self-consistent \( U_I \) and \( V_{IJ} \) using new pseudohybrid functionals for Hubbard interactions [36–39]. We also consider rotationally invariant interactions [38, 40] so that \( U \) and \( V \) for valence \( s \) and \( p \) orbitals of Bi (Sb) and 2\( p \) orbital of O are computed as shown in Table I. Detailed parameters are in Supplementary Materials (SM) [49].

We first discuss the roles of intersite Coulomb interaction in bismuthates and antimonates without doping. At low-temperature, BBO has the monoclinic structure having oxygen octahedra with breathing distortion of displacement by \( \delta_B \) and small tilting angle of \( \theta_T \) between them as shown in Fig. 1(a), while BSO has \( \delta_B \) only, resulting in fcc structure (Fm\( \overline{3} \)m) [24]. To highlight the role of \( V \), we investigate the artificial double-well potential induced by \( \delta_B \) without tilting [Fig.1(b)]. For BBO, our DFT-GGA calculation underestimates \( \delta_B \) with a very shallow potential well [26, 28]. The breathing distortion, however, is significantly enhanced when \( \delta_B \) is considered. Unlike BBO, BSO has a relatively deep potential with DFT-GGA. Nonetheless, the energy gain from the breathing distortion in BSO also becomes larger with the extended Hubbard interactions.

As shown in the model potential wells in Fig. 1 (b), the intersite Hubbard interactions are found to be critical to reproduce experimentally observed CDW states of the undoped cases. Our results on a fully relaxed monoclinic BBO are summarized and compared with the previous studies (Table II). If tilting of \( \theta_T \) is allowed, DFT-GGA accidentally reproduces \( \delta_B \) owing to its overestimation of volume by \( \sim 4\% \) and \( \theta_T \) by \( \sim 14\% \) but still cannot describe the insulating gap of CDW state like a previous work [31]. On the other hand, DFT+\( U+V \) calculation well describes all the critical experimental parameters.

To investigate the effect of extended Hubbard interactions in BBO at higher temperature above the CDW transition, we compute the band structure of BBO in the perfect cubic perovskite phase with experimental volume, using DFT-GGA, DFT+\( U+V \), and GW\( _0 \) methods as shown in Figs. 2 (a) and (b). The width of energy band crossing the Fermi level \( (E_F) \) is enhanced with both DFT+\( U+V \) and GWA compared with one with DFT-GGA. We also note that the DFT-GGA energy bands for fully occupied states associated with oxygen \( p \) orbitals shifted down by including \( U_p^O \) in the DFT+\( U+V \) and by the self-energy corrections in the GW\( _0 \) method.

Effects of intersite interaction are also conspicuous for electronic structures of the CDW state. Figure 2 (c) shows the calculated density of states (DOS) of BBO with the fully relaxed monoclinic CDW structure obtained from each method (Table II) together with previous GW\( _0 \) result and photoemission spectroscopy (PES) data [52, 53]. The two experiments show the quite different positions of the highest PES peak below \( E_F \) (\( −3 \) eV and \( −5 \) eV, respectively), that may originate from the different substrate conditions [53]. As shown in Fig. 2(c), the DOS peak position for oxygen \( 2p \) orbitals from DFT-GGA is significantly off the experimental one. Furthermore, the energy gap of CDW state is absent despite the correct \( \delta_B \). Unlike DFT-GGA results, the DOS using DFT+\( U+V \) well agrees with the experiments and the previous GW\( _0 \) calculation [31]. The \( 2p \) peak position is

### Table I. Calculated \( U \) and \( V \) (in eV) for Ba\( A_x \)O\( _3 \) (\( A = \) Bi and Sb). \( U_{s(p)}^A \), \( U_{p}^O \) is on-site Hubbard parameters of valence \( s(p) \) orbital of \( A(O) \) atom. \( V_{sp(pp)} \) is the intersite Hubbard parameters between \( s(p) \) orbital of \( A \) and \( p \) orbital of \( O \).

| \( A \) | \( U_{s}^A \) | \( U_{p}^A \) | \( U_{p}^O \) | \( V_{sp} \) | \( V_{pp} \) |
|---|---|---|---|---|---|
| Bi | 1.03 | 0.11 | 8.18 | 1.78 | 1.59 |
| Sb | 0.92 | 0.13 | 8.18 | 1.86 | 1.61 |

### Table II. Calculated structural and electronic properties of BBO along with computational and experimental data from previous studies: \( v \): volume, \( \beta \): monoclinic angle, \( \delta_B \): breathing distortion, \( \theta_T \): tilting distortion, and \( E_g \): band gap

| \( v \) (\( \text{\AA}^3 \)) | \( \beta \) (deg) | \( \delta_B \) (\( \text{\AA} \)) | \( \theta_T \) (\( \text{\AA} \)) | \( E_g \) (eV) |
|---|---|---|---|---|
| 81.80 \( \sim \) 82.54 | 90.16 \( \sim \) 90.27 | 0.08 \( \sim \) 0.09 | 10.12 \( \sim \) 10.72 | 0.84 \( \sim \) 1.1 |

| \( \text{Experiments} \) | \( \text{HSE} \) | DFT-GGA | DFT+\( U+V \) |
|---|---|---|---|
| 82.10 | 85.03 | 82.94 |

| References | 22, 50, 51 |

| Reference | 31 |

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![Figure 1](image-url) (a) Atomic model for distorted octahedra in CDW state of BB(S)O. Breathing distortion of \( \delta_B \) and tilting angle of \( \theta_T \) are defined as an averaged length difference between Bi(Sb)-O bonds and as an angle between vertical axes belong to adjacent octahedra, respectively. (b) Double well potential as a function of \( \delta_B \). Blue, red and grey lines indicate DFT-GGA, DFT+\( U+V \) and experiments [24, 50], respectively.
FIG. 2. Energy bands of BBO of cubic perovskite structure obtained from (a) DFT (blue) and DFT+U+V (red) and (b) GW$_0$ method. (c) Density of states for monoclinic CDW structure. Blue, red, and green line indicate DFT, DFT+U+V and previous GW$_0$ results [31], respectively. Empty circles are from photoemission spectroscopy measurements [52, 53].

located at around $-4$ eV, which is in between two experimental results. The band gap is about 1 eV, consistent with the experimental results.

The results so far demonstrate that our new method describes correctly the electronic and structural properties of undoped bismuthate and antimonates without serious computational costs. Thus, it enables the study of the non-local interaction effects on phonons with various K doping levels thoroughly, which could not be done with HSE or GW method easily. From now on, we present the comprehensive phonon dispersions using the frozen phonon techniques [54] with extended Hubbard interactions to examine the structural instability of potassium doped Ba$_{1-x}$K$_x$BiO$_3$ and Ba$_{1-x}$K$_x$SbO$_3$ (BKBO and BKSO). Related computational details are in SM [49].

Figure 3 (a) shows the phonon dispersion and DOS of Ba$_{1-x}$K$_x$BiO$_3$ together with experimental data [55, 56]. Here we focus four representative phonon modes related with CDW states in BKBO and BKSO systems; stretching and in-phase tilting modes at $M$ point and breathing and anti-phase tilting modes at $R$ point. For stretching mode, Bi-O bond length changes along only two axes of oxygen octahedron while it changes along all three axes in the breathing mode. In Fig. 3(a), it is immediately noticeable that the unstable in(anti)-phase tilting mode at M(R) point obtained by DFT-GGA hardens enough to be stable when V is included, agreeing with experiments. Not only low frequency modes, but the high frequency optical branches obtained with V also agree with experiments. Specifically, our result well matches the anomalous dispersion of LO mode along $\Gamma X$ [55, 57, 58] related with the instability toward the charge ordering [57, 58].

We present doping-dependent evolution of frequencies for the selected phonon modes of BKBO and BSBO in Figs. 3(b) and (c). Our calculations with the extended Hubbard interactions fruitfully reflects the measured trends of structural distortions for the both systems. In case of BKBO shown in Fig. 3(b), the breathing mode computed using DFT-GGA becomes to be stable when $x \geq 0.15$ while it does only when $x \geq 0.4$ in the experiments [58–60] and our results with V. BKBO with $x \geq 0.4$ shows SC states without structural distortions [9, 50, 55, 61] while the tilting instabilities still remain in DFT-GGA as shown in Figs. 3 (a) and (b) [34].
is in sharp contrast to complete absence of instability in DFT+U+V results when \( x \geq 0.4 \). Thus, the non-local Coulomb interaction is decisive in capturing the transition between CDW and SC states of BKBO.

As already shown in Fig. 1 (b), the effect of \( V \) is not as crucial in BKSO as it is in BKBO. Nevertheless, our new method makes improvements in describing experimental phase diagram as shown in Fig. 3 (c). For \( x = 0 \) case, DFT-GGA shows the tilting instability in addition to the breathing instability while only the latter is observed in the experiment and our calculation with \( V \), resulting in perfect fcc structure [24]. In addition, CDW phase survives up to higher doping of \( x \approx 0.4 \) in DFT+U+V calculation, which is closer to the experimental phase boundary of \( x \approx 0.5 \), due to the enhanced stretching instability by \( V \). We also note that the inclusion of \( V \) in BKBO enhances the hybridization between Bi and O atoms and that the breathing and stretching mode, which are the most important for SC, become softer by inclusion of \( V \) or Sb substitution, implying the enhancement of \( T_c \) [24].

Finally, we estimate the effects of non-local interactions on \( e-ph \) coupling constant (\( \lambda \)) for the breathing mode that is an important factor for the SC state. Instead of calculating \( \lambda \) explicitly, we compute ‘reduced \( e-ph \) matrix element’ [30, 33, 62], \( D_{\alpha k}^{\text{ph}} = \partial \epsilon_{\mu k} / \partial u_{\alpha q} \) to compare with previous studies based on HSE directly [33, 35]. Here, \( u_{\alpha q} \) is a displacement vector of phonon mode \( \alpha \) with the wave-vector \( q \) and \( \epsilon_{\mu k} \) energy of \( \mu \)th band at \( k \). Specifically, following previous works [33, 35], we obtain the reduced element of \( D_R \) for the energy band crossing the \( E_F \) at \( k \) of L point by the breathing mode at \( q \) of R point (see Fig. S3 in SM [49]).

For both systems, \( D_R \) increases with doping within DFT-GGA as shown in Fig. 4. In sharp contrast to this, the matrix element with \( V \) decreases with increasing \( x \) for BKBO while it remains more or less the same for BKSO. So, the matrix element of the latter becomes larger than that of the former for \( x > 0.3 \). Considering that the coupling can be roughly estimated as \( \lambda \sim (D_{\alpha k}^{\text{ph}} / \omega_{\alpha q})^{2} \) for phonon frequency \( \omega_{\alpha q} \) [30, 33, 62], Fig. 4 implies a higher \( T_c \) of BKSO than BKBO at larger doping levels with \( V \), agreeing with a recent experiment [24]. We also note that our estimations are consistent with two previous HSE results for a few selected dopings [33, 35].

The opposite trends of \( D_R \)’s can be understood by considering intersite interactions under lattice distortions. The paired octahedra with the breathing modes in Fig. 1 have an elongated long bond (LB) and a shrinking short bond (SB) between Bi(Sb) and oxygens [24]. Based on a perturbation theory, \( D_R^{\text{ph}} \) can be written as \( D_R^{\text{ph}} \delta u_B \simeq \varepsilon_{\text{SB}} - \varepsilon_{\text{LB}} - V(n_{\text{SB}} - n_{\text{LB}}) \) where \( \varepsilon_{\text{SB}} \) and \( \varepsilon_{\text{LB}} \) are energy level and density matrix for SB(LB), respectively, and \( \delta u_B \) is the perturbation amplitude of the breathing mode (See SM [49] for detailed derivations). Since \( n_{\text{LB}} > n_{\text{SB}} \) for lower dopings, the intersite interaction should enhance the matrix elements over those from DFT-GGA. As doping level is increased, the difference between \( n_{\text{LB}} \) and \( n_{\text{SB}} \) diminishes so that the effect of nonlocal interactions vanishes as shown in Fig. 4.

In summary, we present a comprehensive study on the doping dependent electronic and structural properties of prototypical charge ordered materials, BKBO and BKSO using a newly developed \( \text{ab initio} \) computational method. We demonstrated that the non-local Coulomb interactions between the nearest neighbours are essential physical parameters in determining the doping dependent evolution of their CDW and SC states, highlighting nontrivial relationships between the nonlocal interaction, charge order and lattice distortion in correlated materials.

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**SUPPLEMENTARY MATERIALS**

**Pseudohybrid density functional for extended Hubbard interactions**

The total energy formula with the extended Hubbard interactions including both on-site and intersite Coulomb interaction (\( U \) and \( V \)) is given by [40]

\[
E_{\text{DFT+U+V}} = E_{\text{DFT}} + E_{\text{UV}},
\]

where \( E_{\text{DFT}} \) is the (semi)local density functional and \( E_{\text{UV}} \) the extended Hubbard functional. Within a rotationally invariant form with the fully localized limit
(FLL) double counting correction, \( E_{UV} \) is written as [40]

\[
E_{UV} = \sum_{I} \sum_{m m' \sigma} \frac{U^I}{2} (\delta_{mm'} - n^{Il}_{mm} n^{Il'}_{m'm'}) - \sum_{(I,J)} \sum_{m m' \sigma} \frac{V^{IJ}}{2} n^{Il}_{mm} n^{Il'}_{m'm'},
\]

where the generalized occupation matrix is \( n^{Il}_{mm'} = \sum_{k \nu} \langle \phi^I_{k \nu} | \psi^I_{m \sigma} \rangle \langle \phi^I_{m' \sigma'} | \psi^I_{k \nu} \rangle \), \( f_{k \nu} \) the Fermi-Dirac function of Kohn-Sham orbital of \( \psi^I_{k \nu} \) of the \( \nu \)th band with spin \( \sigma \) at momentum \( k \), and \( \phi^I_{m \sigma} \) the localized orbitals with angular quantum number \( m \). Here, \( I \) and \( J \) are abbreviated indexes for atomic positions and principal and azimuthal quantum numbers together. \( \{ I, J \} \) in Eq. S2 denotes a pair of atoms within the nearest neighboring distances.

Following the ansatz by Mosey et al. [63, 64], we extend the ACBN0 pseudohybrid functional for \( U \) [36] into \( V \) [38] by considering the renormalized occupation number \( \frac{1}{2} n^{Il}_{mm} \) and density matrix \( P^{Il}_{mm'} \) for a pair of different atoms \( I \) and \( J \):

\[
\begin{align*}
N^{Il}_{mm'} &= \sum_{I} \sum_{m' \sigma} \langle \psi^I_{m \sigma} | \phi^I_{m' \sigma} \rangle \langle \phi^I_{m' \sigma} | \psi^I_{k \nu} \rangle, \\
P^{Il}_{mm'} &= \sum_{k \nu} f_{k \nu} N^{Il}_{mm'} \langle \psi^I_{k \nu} | \phi^I_{m \sigma} \rangle \langle \phi^I_{m' \sigma} | \psi^I_{k \nu} \rangle,
\end{align*}
\]

where \( w_k \) is \( k \)-point weight and \( f_{k \nu} \) is the Fermi-Dirac function of the Bloch state \( | \psi^I_{k \nu} \rangle \). By using Eq. S3 and S4, \( U^I \), \( J^I \), and \( V^{IJ} \) can be defined as [36, 38, 39]:

\[
\begin{align*}
U^I &= \sum_{m \cdots m''} \sum_{\sigma \sigma'} P^{Il}_{mm} P^{Il'}_{m'm''}(mm' | m''m'') \\
J^I &= \sum_{m \cdots m''} \sum_{\sigma \sigma'} \delta_{\sigma \sigma'} P^{Il}_{mm} P^{Il'}_{m'm''}(mm' | m''m''), \\
V^{IJ} &= \frac{1}{2} \sum_{m \cdots m''} \sum_{\sigma \sigma'} [P^{Il}_{mm} P^{Il'}_{m'm''} - \delta_{\sigma \sigma'} P^{Il}_{mm} P^{Il'}_{m'm''}](mm' | m''m'') - \delta_{\sigma \sigma'} P^{Il}_{mm} P^{Il'}_{m'm''} | mm' | m''m''
\end{align*}
\]

where \( (mm' | m''m'') = \int dr_1 dr_2 \phi^I_{m \sigma}(r_1) \phi^I_{m' \sigma}(r_1 - r_2) \phi^I_{m'' \sigma'}(r_2) \phi^I_{m''' \sigma'}(r_2) \).

**Calculation details**

We implemented the pseudohybrid density functionals for extended Hubbard interactions shown in Eqs. S5, S6, and S7 in QUANTUM ESPRESSO package [38, 46, 65]. We used the norm-conserving pseudopotentials provided by the PseudoDojo project [66]. The energy cutoff for charge density was set to 480 Ry. A 15×15×15 \( k \)-point mesh was used for self-consistent calculation of perfect perovskite structure (5 atoms in the unitcell). The \( k \)-mesh density was kept the same for all other calculations. The Hubbard \( U \) and \( V \) parameters are obtained during the self-consistent calculation from Eqs. S5, S6 and S7 as shown in Table S1.

The potassium (K) substitution effects are simulated by reducing the number of electrons in the unitcell and inserting a compensating background charge. For lattice optimization with doping, we used large cubic supercell structures containing 40 atoms to model realistic doping. As shown in Fig. S1, our optimized pseudocubic lattice parameter of \( a_p \) using DFT+\( U \)+\( V \) formalism agrees with experimental data [24, 50] very well while DFT-GGA fails. With these optimized structures, the phonon dispersions were calculated using the finite displacement method by Phonopy [54]. Full phonon band structures of BKBO and BKSO are shown in Fig. S2.

For the direct comparison with the previous HSE result (Fig.4 of main text), the reduced matrix element for \( e^-pH \) interaction is obtained by using the same scheme used in Ref. 33. For example, the breathing distortion induces band splitting as shown Fig. S3. The energy splitting at L point (\( \Delta E \)) is used to determine the matrix element with the given oxygen displacement.
TABLE S1. Calculated $U$ and $V$ (in eV) for Ba$A_{1-x}$K$_x$O$_3$ ($A=$ Bi and Sb). $U_{sp}(p)$ ($U^{Ba}_{pp}$) is on-site Hubbard parameters of valence $s(p)$ orbital of $A$(O) atom. $V_{sp(pp)}$ is the inter-site Hubbard parameters between $s(p)$ orbital of $A$ and $p$ orbital of O. $V^{Ba}_{sp}$ is the inter-site Hubbard parameters of between $s$ orbital of Ba and $p$ orbital of O.

\[
\begin{array}{cccccc}
| x | U^{Ba}_{x} & U^{Bi}_{x} & U^{DO}_{x} & V_{pp} & V^{Ba}_{sp} & U^{3B}_{x} & U^{3B}_{p} & U^{O}_{x} & V_{pp} & V^{Ba}_{sp} \\
|---|---|---|---|---|---|---|---|---|---|---|
| 0.00 | 1.03 0.11 8.18 1.88 1.99 0.74 | 0.92 0.13 8.38 1.88 1.61 0.75
| 0.05 | 1.00 0.11 8.17 1.87 1.58 0.76 | 0.95 0.13 8.35 1.82 1.59 0.74
| 0.10 | 0.98 0.11 8.15 1.74 1.58 0.75 | 0.91 0.13 8.12 1.78 1.58 0.74
| 0.15 | 0.96 0.11 8.14 1.72 1.57 0.75 | 0.88 0.13 8.08 1.74 1.56 0.73
| 0.20 | 0.94 0.11 8.13 1.70 1.56 0.74 | 0.85 0.13 8.05 1.71 1.55 0.72
| 0.25 | 0.92 0.11 8.11 1.68 1.56 0.74 | 0.83 0.12 8.01 1.68 1.54 0.71
| 0.30 | 0.90 0.11 8.09 1.66 1.55 0.73 | 0.80 0.12 7.97 1.65 1.52 0.71
| 0.35 | 0.89 0.11 8.08 1.64 1.54 0.72 | 0.78 0.12 7.93 1.63 1.51 0.69
| 0.40 | 0.87 0.11 8.06 1.63 1.54 0.72 | 0.76 0.12 7.89 1.60 1.49 0.68
| 0.45 | 0.85 0.10 8.04 1.61 1.52 0.72 | 0.74 0.12 7.84 1.58 1.48 0.68
| 0.50 | 0.83 0.10 8.02 1.59 1.52 0.70 | 0.72 0.12 7.79 1.55 1.46 0.67
| 0.55 | 0.81 0.10 8.00 1.57 1.51 0.70 | 0.70 0.12 7.74 1.53 1.44 0.66
| 0.60 | 0.80 0.10 7.98 1.56 1.50 0.69 | 0.68 0.12 7.69 1.51 1.43 0.65
\end{array}
\]

Doping dependence of the reduced el-ph matrix elements

The essential trend of the K doping ($x$) dependent variation of the reduced el-ph matrix ($D^L_R$) of Ba$_{1-x}$K$_x$O$_3$ ($A=$Bi, Sb) shown in Fig. 4 of the main text can be understood by considering simplified perturbative expansions of interactions within DFT+$U$+$V$ scheme. The extended Hubbard interactions are treated as perturbations to the Kohn-Sham (KS) equation of (semi)local functional such that

\[
\mathcal{H}_{\text{total}} = \mathcal{H}_{\text{DFT}} + \mathcal{H}_{\text{UV}} \tag{S8}
\]

\[\mathcal{H}^\text{el-ph}_{\text{total}} = \mathcal{H}^\text{el-ph}_{\text{DFT}} + \mathcal{H}^\text{el-ph}_{\text{UV}} + \mathcal{H}^\text{el-ph}_{\text{DFT}} = \mathcal{H}^\text{el-ph}_{\text{DFT}}(\mathcal{V}^\text{el-ph})\]

where $\mathcal{H}_{\text{total}}^{\psi_{\kappa\nu}^e} = \mathcal{H}^\text{el-ph}_{\text{DFT}} = \mathcal{H}^\text{el-ph}_{\text{DFT}}\mathcal{V}^\text{el-ph}$. Here, $\mathcal{V}^\text{el-ph}$ is the KS potential corresponding to (semi)local energy functional ($E_{\text{DFT}}$) and $\psi^e_{\kappa\nu}$ the KS wavefunction with eigenvalue of $\varepsilon^e_{\kappa\nu}$. The perturbation can be written as $\mathcal{H}_{\text{UV}}^{\psi_{\kappa\nu}^e} = \delta E_{\text{UV}} / \delta (\psi_{\kappa\nu}^e)$. As discussed above, we only consider the alternation of energy bands crossing the Fermi level at the L point in the presence of breathing distortion at the R point as shown in Fig S3 so that the momentum, spin and band indexes will be dropped hereafter.

The energy band considered here mainly originate from the anti-bonding state between s orbital of Bi (Sb) at the center of octahedra and p orbitals of oxygen at their vertices [67]. Thus, the pair of distorted perovskites (see Fig. 1a of the main text) has elongated and shortened bonds for the anti-bonding states. We will call them the long and short bonding (LB and SB), respectively. From these considerations, the split energies of the band by the breathing mode in Fig. S3 can be approximated as energy eigenvalues of $\epsilon_{\text{LB}}$ and $\epsilon_{\text{SB}}$ (or $\epsilon_{\text{LB}}$ and $\epsilon_{\text{SB}}$ without $\mathcal{H}_{\text{UV}}$) for the static atomic configurations associated with LB and SB, respectively. The resulting difference of $\epsilon_{\text{SB}} - \epsilon_{\text{LB}}$ (or $\epsilon_{\text{SB}} - \epsilon_{\text{LB}}$ without $\mathcal{H}_{\text{UV}}$) can be assigned as $D^L_R$ because the energy level of the anti-bonding SB is higher than that of the LB.

With the amplitude $\delta u_B$ of the breathing mode, the $E_{\text{DFT}}$ contribution is simply written as $D^L_R \cdot \delta u_B = \epsilon_{\text{SB}} - \epsilon_{\text{LB}}$. In case of a pristine octahedron, we can assign an overlap integral ($t_{sp}$) between p orbital of oxygen and s orbital of Bi(Sb) and the orbital energies for them as $\omega_p$ and $\omega_s$, respectively. Then, with distorted structures by the breathing mode, the energy splitting can be expressed

FIG. S2. Phonon band structures of BKBO and BKSO. Blue and red lines indicate DFT and DFT+$U$+$V$ results, respectively.

FIG. S3. Electronic band structure of Ba$_{0.6}$K$_{0.4}$BiO$_3$ with and without the oxygen-breathing displacement obtained from DFT+$U$+$V$. The breathing distortion induces band splitting dipicted by orange dotted lines. The band splitting of $\Delta E$ indicated by the arrow are used to calculate the reduced e-ph matrix element of $D^L_R$. 

up to the second order of $t_{sp}$ as follows,

$$D^L_R \delta u_B = \varepsilon_{SB} - \varepsilon_{LB} \sim \frac{4t_{sp}^2 \delta \tau_{sp}}{|\omega_p - \omega_s|} , \quad (S9)$$

where $t_{sp}$ changes to $t_{sp}(1 \pm \delta \tau_{sp})$ for SB (LB) and $|\omega_p - \omega_s| \gg t_{sp}$ is assumed. We note that the K doping ($x$) enhances the hole contribution to the $p$ orbital, thereby reducing the $|\omega_p - \omega_s|$. So, Eq. S9 implies that $D^L_R$ based on DFT-GGA increases with $x$, explaining the increasing matrix elements shown in Fig. 4. We also note that a small contraction of lattice constant with doping in Fig. S1 also could increases $t_{sp}$, thus corroborating the trend.

With onsite and intersite Hubbard interaction for $s$ orbital of Bi(Sb) and $p$ orbital oxygen ($U_p$ and $V_{sp}$), the perturbative Hamiltonian for the Hubbard interactions can be written as

$$H_{UV} = H_U + H_V = U_p(1 - 2n_{pp}) - V_{sp}n_{sp} , \quad (S10)$$

where $n_{pp}$ is the density matrix for the $p$ orbital of oxygen and $n_{sp}$ the generalized one for the neighboring $s$ orbital of Bi(Sb) and oxygen $p$ orbitals. Here, the spin index is suppressed and the significantly smaller onsite energy for the $s$ orbital as shown in Table. S1 is neglected. For $n_{pp} \neq 0$, the onsite Hubbard energy shifts the oxygen level of $\omega_p$ toward $\omega_s$ so that, according to Eq. S9, the resulting $D^L_R$ should enhance compared with those from DFT-GGA and increases as the amount of doped potassium accumulates. This tendency is indeed confirmed by our calculation only with $U$ as shown in Fig. S4.

From Eq. S10, we can estimate the contribution from the nonlocal interactions for the matrix element as follows,

$$D^L_R \delta u_B = \varepsilon_{SB} - \varepsilon_{LB} \sim \bar{\varepsilon}_{SB} - \bar{\varepsilon}_{LB} - V_{sp}(n^{SB}_{sp} - n^{LB}_{sp}) , \quad (S11)$$

where $\bar{\varepsilon}_{SB(LB)}$ is the renormalized energy level of Eq. S9 by the on-site energy of $U_p$ in Eq. S10 and $n^{SB(LB)}_{sp}$ is the generalized density matrix for the SB (LB). Here we note that we neglect the perturbation to the wave function in considering Eq. S11 that seems to be smaller than the variations of density matrix under perturbations. The density matrix for the lower energy state should be larger than that for the higher, i.e., $n^{LB}_{sp} > n^{SB}_{sp}$ so that Eq. S11 immediately implies the enhanced $D^L_R$ with $V$ as shown in Fig. 4 of the main text. Furthermore, as doping increases, the charge disproportionation or difference between the SB and LB should decreases and then disappear as $x$ approaches 1. Therefore, $n^{SB}_{sp} - n^{LB}_{sp}$ in Eq. S11 decreases to zero as doping increases so that the effect of intersite Hubbard interactions to $D^L_R$ diminishes as $x$ increases as shown in Fig. 4.

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