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Ternar ABX_3 pero ki e made of corner- haring BX_6 oc ahedra ha e long fea red prominen l in olid- a e chemi r and conden ed ma er ph ic . S ill, he join nder anding of heir o main bgro p —***halides and oxides***—ha no been f ll de eloped. Indeed, nlike he ca e in impler compo nd ha ing a ingle, rob repea ed mo if ("monomorpho "), cer ain c bic pero ki e can manife a non- hermal (= in rin ic) di rib ion of local mo if ("pol morpho ne ork "). S ch a ic deforma ion can incl de po i ional degree of freedom (e.g., a omic di placemen and oc ahedral il ing) or magne ic momen degree of freedom in paramagne . Unlike hermal mo ion, ch a ic di or ion do no ime-a erage o ero, being an e pre ion of he in rin ic mme r breaking preference of he chemical bonding. The pre en d compare elec ronic r c re fea re of o ide and halide pero ki e ar ing from he a ic pol morpho di rib ion of mo if de cribed b Den i F nc ional Theor (DFT) minimi a ion of he in ernal energ , con in ing o fini e empera re hermal di order modeled ia fini e empera re DFT molec lar d namic . We find ha (i) differen ***oxide vs. halide*** ABX_3 compo nd adop differen energ -lo ering mme r -breaking mode . The calc la ed pair di rib ion f nc ion (PDF) of $SrTiO_3$ from he fir -principle agree i h recen l mea red PDF. (ii) In bo h o ide and halide , ch a ic di or ion lead o band gap ***blueshifts*** i h re pec o ndi or ed c bic ***Pm-3m*** r c re. (iii) For o ide pero ki e , high- empera re molec lar d namic im la ion ini ia ed from he a icall di or ed pol morpho r c re re eal ha he

Introduction

ABX_3 halide $A^{(I)}B^{(IV)}X_3^{(VII)}$ and oxide ABO_3 perovskite often crystalize as corner-sharing low-symmetry (e.g., orthorhombic or tetragonal) phases at low temperatures (LT), sometimes transforming at higher temperatures into the cubic phase. They are generally discussed in terms of the nature of the microscopic degree of freedom, be that the magnetic moments (in ferromagnet/paramagnet), or electric dipoles (in ferroelectric/paraelectric), or octahedral degrees of freedom (e.g., tilting and rotations) [1–5]. X-ray diffraction (XRD) measurements [6] on such cubic

Initially, in this approach, the disorder in the para-phases was treated by "structural approximants" avoiding molecular dynamics (MD). Notable examples include the “Virtual Crystal Approximation” (VCA) [49] and “Coherent Potential Approximation” (CPA) [50]. These approaches offer an effective configuration that could be used as input to standard electronic structure theory and capture some aspects of disorder. Whereas such models are ubiquitous for positionally disordered alloys, they are not gen-

the distortions related to different Goldschmidt factor and band-edge states. In this paper, we mainly focus on the semiconductor oxide ABO_3 (A = Ba, Sr, Ca, Pb; B = Ti, Zr), and halide $CsBX_3$ (B = Ge, Sn, Pb; X = F, Br, I), $KPbI_3$ and $RbPbI_3$, and show three

ful “structural approximants” for describing the electronic structure of realistic cubic perovskites before thermal agitation sets in. The thermally induced disorder is then added at the DFT molec-

gap by taking $ATiO_3$ (A^+ = Ca, Sr, Ba) and $CsBI_3$ (B^{2+} = Pb, Sn) as examples.

The multi-mode distortions can lower the energy more than the single-mode distortions because of a few reasons. First, instead of having a single-mode with a large, uniform tilting angle and/or displacement throughout the lattice, it is sometimes energetically advantageous to have a few modes covering a range of tilting angles or displacements. Given the similar energy lowering for a single-mode distortion with a large tilting angle and a few modes with small tilting angles, we anticipate that modes such as $a^-a^-a^-$, $a^0a^0b^-$ and $a^0b^-b^-$ modes in $SrTiO_3$, $a^0a^0b^-$ and $a^0a^0b^+$ modes in $CsPbI_3$, as well as $a^-a^-a^-$, $a^0b^-b^-$, and $a^-a^-a^+$ modes in $CaTiO_3$ would coexist. The similar energy lowering of different single-mode distortions might lead to a mixture of different tilting modes with energy lowering. Indeed, as depicted in Fig. 1, the mixture mode $(a^0a^0b^-)_1^2$ $(a^0a^0b^+)_2^3$ $(a^0a^0b^-)_3^4$ in 4 × 4 × 4 supercell of the cubic $SrTiO_3$ has slightly lower energy (by 1 meV/f.u.) than the 2 × 2 × 2 supercell with the single a

TABLE 2

The DFT energy lowering ΔE_{M-P} due to multi-mode distortions in polymorphous structures compared with the energy of the nominal cubic (Pm-3m) structure was calculated by using the PBEsol functional. These polymorphous structures with multi-mode distortions were obtained by minimization of internal forces of the nudged, cubically shaped 4

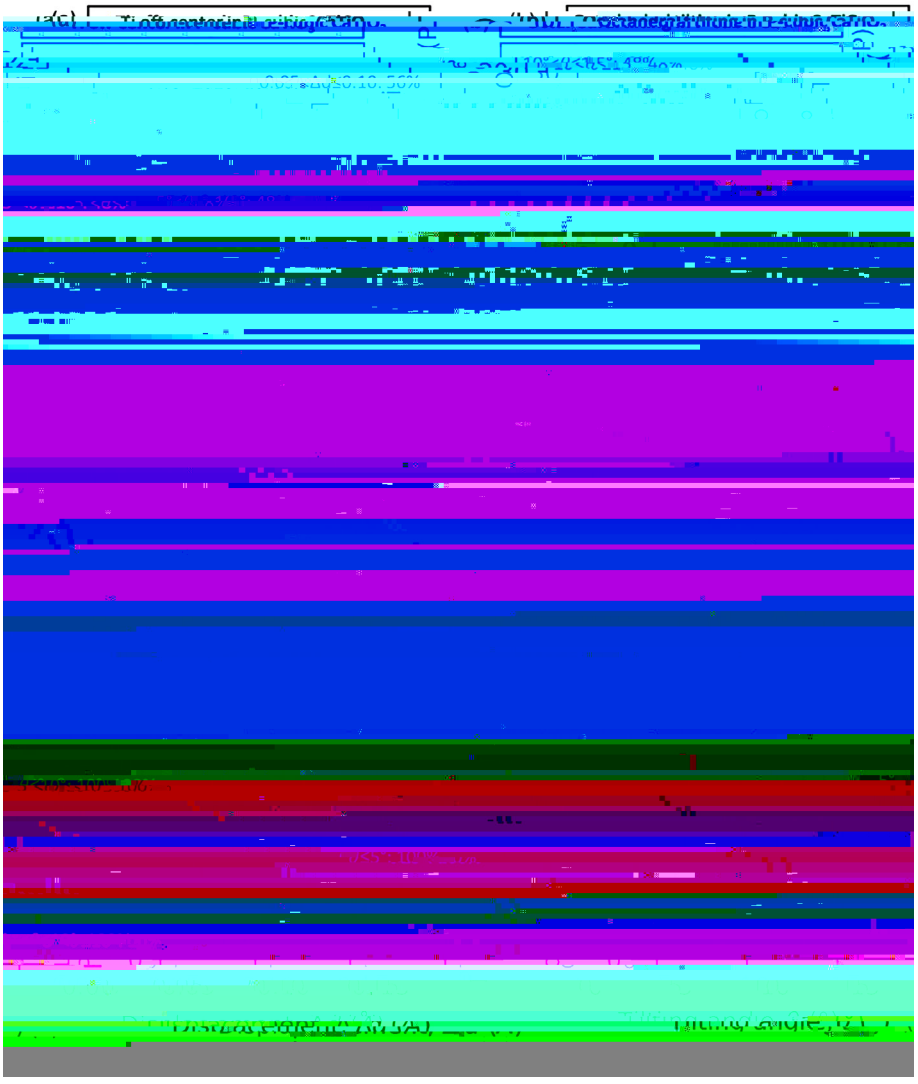


FIGURE 3

atomic distances and short-range order. This information, not addressed in the present paper, awaits to be mined in the form of SRO parameters and PDF data as reported in Ref. [28]. The PDF is a local probe that reflects the distribution of atom–atom distances, thus a good way to determine the local atomic configurations and distortion of local motifs within the system. As already noted, fitting the diffraction data in the Rietveld process to a single formula cubic (Pm-3m) cell [72] can miss the existence of intrinsic DOWPs that evidently lead to energy lowering (Fig. 1

5p at VBM and Pb-6p – I-5p at CBM as illustrated in Fig. 8d). We find that the octahedral rotation in $CaTiO_3$

To analyze the relationship between the direct gap component and the rotation DOWPs, Fig. 9b shows several cubic $SrTiO_3$ with frozen-in $a^0b^-b^-$ mode with a rotation angle of 0°, 2.5°, and 5°. The increase in rotation amplitude causes the VBM spectral intensity at Γ to increase, but VBM spectral intensity at R diminishes. These trends signal the buildup of a significant direct band gap component in cubic $SrTiO_3$ due to tilting DOWPs.

D. Effects of single-mode and multi-mode static non-thermal deformations on band gaps

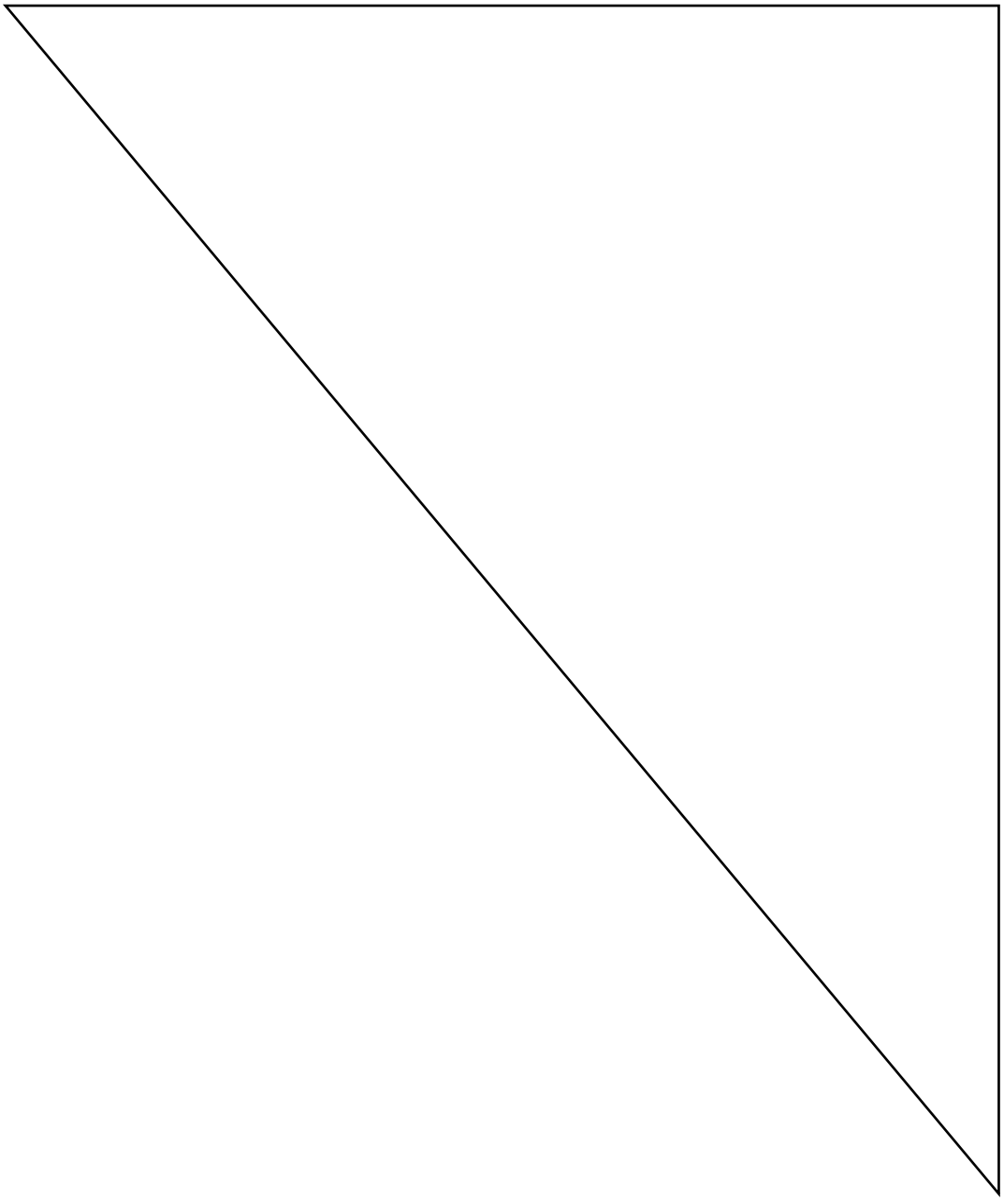
Fig. 10 summarizes for several cubic ABX_3 compounds (i) the minimal band gap from monomorphous (Pm-3m) cell (shown in blue), (ii) the gap resulting from allowing single-mode DOWPs

multi-mode DOWPs in polymorphous network show much larger blueshift values from 0.11 eV for $BaTiO_3$ to 0.55 eV for $CsSnI_3$. Local symmetry breaking, either single-mode or multi-mode DOWPs, can lead to significant band gap blueshift.

Effect of temperature-induced distortion in molecular dynamics on band gaps

A. DFT molecular dynamics: Temperature-enhanced deformations in $CaTiO_3$ and $SrTiO_3$

The free energy of the vibrating lattice $F = U_0 - TS$ at finite temperature can be studied using MD simulations. As the tem-



mally enhanced atomic displacements at finite temperatures are consistent with enlarged Li displacements (rather than diminished displacements) as temperature increase in paraelectric $LiNbO_3$ [39].

B. The effects on band gap shift due to thermal distortion in oxide perovskites

The enhanced thermal motions revealed by the AIMD simulations result in significant band gap changes. For instance, the averaged band gap (expressed as $\sum_{i=1}^{N} E_g(S_i)/N$ of individual configuration S_i along the thermodynamic equilibrium trajectory $E_g(S_i)$ refers to the allowed and forbidden band gap of S_i) and S_i) for cubic $CaTiO_3$ and $SrTiO_3$ are shown in Table 1. The band gap redshift due to thermal motions at 2000 K in cubic $CaTiO_3$ is 1.15 eV with respect to polymorphous structure, and 0.77 eV with respect to the nominal cubic structure. Similarly, in cubic $SrTiO_3$, the corresponding band gap redshifts are 0.72 eV and 0.49 eV, respectively, at 1400 K. Evidently, thermal motions in cubic $CaTiO_3$ and $SrTiO_3$ lead to significantly band gap redshift

Table 1 provides both a preview and a succinct summary of the main differences between the effects of static non-thermal vs. dynamic thermal displacements on band gaps for oxide perovskites.

For oxide perovskites: Different from nominal cubic $SrTiO_3$ and $CaTiO_3$ with p-like VBM and d-like CBM, the "correlated" Mott insulators having

at high temperature ($>T_c$) compared with band gap at T = 0 (monomorphous structure).

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