Narrow Bandgap in $\beta$-BaZn$_2$As$_2$ and Its Chemical Origins

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ABSTRACT: $\beta$-BaZn$_2$As$_2$ is known to be a $p$-type semiconductor with the layered crystal structure similar to that of LaZnAsO, leading to the expectation that $\beta$-BaZn$_2$As$_2$ and LaZnAsO have similar bandgaps; however, the bandgap of $\beta$-BaZn$_2$As$_2$ (previously-reported value $\sim$0.2 eV) is one order of magnitude smaller than that of LaZnAsO (1.5 eV). In this paper, the reliable bandgap value of $\beta$-BaZn$_2$As$_2$ is determined to be 0.23 eV from the intrinsic region of the temperature dependence of electrical conductivity. The origins of this narrow bandgap are discussed based on the chemical bonding nature probed by 6 keV hard X-ray photoemission spectroscopy, hybrid density functional calculations, and the ligand theory. One origin is the direct As-As hybridization between adjacent [ZnAs] layers, which leads to a secondary splitting of As 4p levels and raises the valence band maximum. The other is that the non-bonding Ba 5$d$2,5,2 orbitals form unexpectedly deep conduction band minimum (CBM) in $\beta$-BaZn$_2$As$_2$, although the CBM of LaZnAsO is formed mainly of Zn 4s. These two origins provide a quantitative explanation for the bandgap difference between $\beta$-BaZn$_2$As$_2$ and LaZnAsO.

INTRODUCTION

Layered mixed-anion compounds including LaCuChO ($Ch = S, Se, Te$) and $\beta$-BaAsO (for $M = Mn, Zn; \ Pn = P, As$) and $\beta$-BaZn$_2$P$_2$O ($T' = Fe, Ni; \ Pn = P, As$) exhibit a wide variety of electronic phenomena such as wide gap $p$-type semiconduction and superconductivity, making them attractive for a new platform to explore functional materials. These compounds have the general chemical formula $LnMAX$ ($Ln$ = lanthanide, $M$ = transition metal, $A$ = chalcogen or pnictogen, $X$ = O, F or H), which are called ‘111-type’ compounds and have the tetragonal ZrCuSiAs-type structure (space group $P4/nmm$). In particular, an interesting feature of these compounds is that they have a two-dimensional crystal structure composed of alternating $[MA]$ and $[LnX]$ layers; the former forms a carrier conduction path and the latter forms a wider bandgap than the conduction layer and behaves like a carrier transport barrier.

On the other hand, similar layered-structure compounds (i.e., composed of a narrow bandgap $[MA]$ layer) have also been found; a representative one is called ‘122-type’ compounds expressed by the chemical formula $AeM_2Pn_2$ ($Ae$ = alkaline earth). Similar to the 111-type compounds, the properties of $AeM_2Pn_2$ change drastically if the type of the transition metal $M$ is varied. For example, $AeM_2Pn_2$ behave as superconductors (for Fe$^{0,58}$ and Ni$^{95}$), ferromagnetic metals (for Co$^{66}$), antiferromagnetic metals (for Cr$^{95}$), diamagnetic metals (for Cu$^{14}$), antiferromagnetic semiconductors (for Mn$^{15,98}$), and non-magnetic semiconductors (for Zn$^{99}$). Most of them crystallize into the tetragonal ThCr$_2$Si$_2$ structure with the space group $I\bar{4}/mmm$. On the other hand, BaZn$_2$As$_2$ has two crystalline phases; the low-temperature orthorhombic phase $\alpha$-BaZn$_2$As$_2$ (for Cu$^{94}$, $\alpha$-BaCu$_5$S$_2$-type structure, the space group $Pnma$) and the high-temperature tetragonal phase $\beta$-BaZn$_2$As$_2$ (the 122-type one, the space group $I\bar{4}/mmm$) (Fig. 1(a)). Recently, $(Ba_{x-0.5}K_x)(Zn_{1-x}Mn_x)As_2$ was reported to be a good diluted magnetic semiconductor, in which the tetragonal phase is stabilized by doping of 10% K or Mn$^{99}$.

It is known that the anion-anion chemical bonding influences the ground states of 122-type compounds significantly and is intertwined with the formation of the ferromagnetic quantum critical point and superconductivity.$^{23,24}$ In our previous work, we roughly determined the bandgap of a $\beta$-BaZn$_2$As$_2$ epitaxial film to be $\sim$0.2 eV from optical transmission spectra, which is extremely narrow compared with that of the similar 111-type compound, LaZnAsO (1.5 eV). Further it has been reported that simple zinc arsenides have much larger bandgaps as well (e.g., 0.99 eV for Zn$_3$As$_2$ and 0.98 eV for ZnAs$_2$). Recently, first-principles calculations for the $\alpha$- and $\beta$-BaZn$_2$As$_2$ phases reported that they have complicated and highly-anisotropic electronic structures due to the unusual cation-anion and anion-anion hybridizations, however, it does not provide an explanation for the extreme narrow bandgap of $\beta$-BaZn$_2$As$_2$. Further, the previously-reported bandgap value is not so reliable due to the interference
of the substrate optical absorption, and no other experimental data on its electronic structure has been provided.

In this work, we determined the bandgap of $\beta$-BaZnAs$_2$ from the carrier transport properties and obtained the reliable electronic structure by hard X-ray photoemission spectroscopy (HAXPES). Hybrid density functional theory calculations with Heyd-Scuseria-Ernzerhof (HSE06) functionals provided good agreement with the experimental bandgap and the valence band (VB) HAXPES spectra. We found the anion-anion hybridization between adjacent [ZnAs] layers induces a secondary splitting of the outer orbitals of As atoms and widens the VB. In addition, the $d$ orbitals of the heavy alkaline earth Ba ion form a deep conduction band (CB) minimum (CBM) due to non-bonding nature of the Ba 5$d_{2}$-$2$ orbitals. These two factors provide a quantitative explanation for the narrow bandgap of $\beta$-BaZnAs$_2$.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

Synthesis of powder and polycrystalline samples. Polycrystalline samples of $\beta$-BaZnAs$_2$ and LaZnAsO were synthesized through solid-state reactions. First, BaAs and LaAs precursors were synthesized from stoichiometric mixtures of Ba, La, and As pieces / powders, which were sealed in evacuated silica-glass ampules and heated at 700 °C for 20 hours. Then, stoichiometric BaAs, Zn, and As powders (for $\beta$-BaZnAs$_2$) and stoichiometric LaAs and ZnO powders (for LaZnAsO) were mixed, respectively, and pre-heated at 700 °C in evacuated silica-glass ampules. The reaction products were ground and pressed into pellets and annealed at 1000 °C for 20 hours in evacuated silica-glass ampules again. After annealing, the ampule containing LaZnAsO was furnace-cooled to room temperature (RT); while that containing BaZnAs$_2$ was rapidly quenched by dropping into water to stabilize the high-temperature phase, $\beta$-BaZnAs$_2$. All the synthesis processes except the sealing, the heating and the cooling processes were carried out in a glove box filled with dry argon gas (dew point < -90 °C, O$_2$ < 1 ppm).

Structural and electronic measurements. The phase determination of the obtained samples was carried out by powder x-ray diffraction (PXRD) (D8 ADVANCE, Bruker, using Cu Ka rotating anode). PXRD patterns were simulated from literature structures$^{22,29}$ using a TOPAS code.$^{30}$ The temperature ($T$) dependence of dc electrical conductivity ($\sigma$) of the $\beta$-BaZnAs$_2$ sample was measured by the conventional four-probe method with a physical property measurement system (PPMS, Quantum Design) up to 400 K. HAXPES measurements were performed at the BL15XU undulator beamline ($h\nu$ =5953.4 eV) of SPring-8 at RT,$^9$ where the binding energy is measured from the Fermi level calibrated using a reference spectrum measured on a gold thin film. Total energy resolution was set to 2.40 meV, which was confirmed by the Fermi cut-off of the gold thin film.

Theoretical calculations. Density functional theory (DFT) and hybrid DFT (HDF) calculations were performed using the projector augmented plane-wave method implemented in the Vienna Ab initio Simulation Program (VASP 5.3).$^{31}$ The plane wave cutoff energy was set to 345.9 eV. A 5x5x2 k-mesh was used for tetragonal $\beta$-BaZnAs$_2$ and LaZnAsO, and a 5x5x3 k-mesh for trigonal $\beta$-ZnAs$_2$ crystals ( $\beta$-ZnAs$_2$ =Ba, Sr and Ca). For the exchange-correlation functional, we first examined the Perdew-Burke-Ernzerhof (PBE06)$^{32}$ generalized gradient approximation (GGA) functionals; however, we found it underestimated the bandgaps of $\beta$-BaZnAs$_2$ and LaZnAsO. We then examined hybrid functionals and found the HSE06$^{34,35}$ hybrid functionals with the standard mixing parameter of 25% for the exact-exchange term provided reasonable results. Before the electronic structure calculations, variable-cell structure relaxations were performed using the respective functionals.

RESULTS AND DISCUSSION

Crystal structure difference between $\beta$-BaZnAs$_2$ and LaZnAsO. Figures 1(a, b) show the crystal structures of $\beta$-BaZnAs$_2$ and LaZnAsO, respectively, and Fig. 1(d) shows measured & simulated PXRD patterns for the synthesized BaZnAs$_2$ and LaZnAsO samples. All the diffraction peaks of the BaZnAs$_2$ were reproduced well from the ThCr$_2$Si$_2$-type structure (I$\bar{4}$mm) as reported,$^{22}$ substantiating that the metastable $\beta$-BaZnAs$_2$ phase was successfully obtained by the rapid quenching method. The crystal structure of LaZnAsO was confirmed to be the ZrCuSiAs-type one (P4/nmm) as reported.$^{29}$ The literature structural parameters for $\beta$-BaZnAs$_2$ and LaZnAsO are summarized in Table S1 (see Supporting Information). The structures of the [ZnAs] layers are almost the same between $\beta$-BaZnAs$_2$ and LaZnAsO, in which each (ZnAs)$_4$ tetrahedron is connected with four neighboring (ZnAs)$_4$ tetrahedra by sharing their edges in the two-dimensional [ZnAs] layer. On the other hand, we can find a distinct difference between these structures in Fig. 1(e), where the coordination numbers of As atoms around an As atom is plotted as a function of As–As distances, $d_{\text{As–As}}$. The intralayer As–As distances (i.e., $d_{\text{intra}}$ and $d_{\text{inter}}$ as denoted in Figs. 1(a)) are similar between $\beta$-BaZnAs$_2$ and LaZnAsO ($0.410$–$0.425$ nm); whereas, the interlayer As–As distance ($d_{\text{inter}}$ for $\beta$-BaZnAs$_2$ ($0.370$ nm) is much shorter than that for LaZnAsO ($0.660$ nm) due to the different heights between the Ba ion and the LaO layer.
The act of ionization of donors, and attributed e.g. to the variable range hopping (VRH) model, can be expressed by 
\[ \sigma(T) = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) + \sigma_{\text{vrh}} \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right], \]
where the latter express the VRH model with constants \( \sigma_{\text{vrh}} \) and \( T_0 \) as drawn by red curve. The fit gave intrinsic \( E_a \) value of 0.114 eV, which is comparable to those reported for \( \text{BaMn}_2\text{P}_2 \) (0.07 eV),\(^{23}\) \( \text{BaMn}_2\text{As}_2 \) (0.03 eV)\(^{28}\) and \( \text{BaMn}_2\text{Sb}_2 \) (0.03 - 0.10 eV)\(^{28}\) (note that these crystals have the same 122-type structure). Thus we conclude that the intrinsic \( E_a \) is 0.114 eV and thus the bandgap is \( E_g = 2E_a = 0.23 \) eV. We would like to note that the change of the slope in the Arrhenius plot around 1/\( T \) ~ 0.07 seems very abrupt and might suggest a phase transition; however, the fitting result to the combined model shows that the experimental transition is duller than that expected from the theoretical model.

We also calculated the bandgaps for \( \beta\text{-BaZn}_2\text{As}_2 \) and \( \text{LaZnAsO} \) by DFT calculations. First, we examined the PBE96 GGA functional, but it gave a negative bandgap for \( \beta\text{-BaZn}_2\text{As}_2 \) and an underestimated value of 0.56 eV for \( \text{LaZnAsO} \), which are consistent with the reported GGA results.\(^{4,25,28}\) It is caused by a well-known bandgap problem of DFT in which bandgaps are in general underestimated from experimental values. Then, we examined the HSE06 hybrid functional and found that it provided reasonable bandgaps of 0.23 eV for \( \beta\text{-BaZn}_2\text{As}_2 \) and 1.38 eV for \( \text{LaZnAsO} \), which are fairly close to the experimental values. Besides, HSE06 also gave better structural parameters than PBE96 (see Table S1 in Supporting Information).

Electronic structure differences between \( \beta\text{-BaZn}_2\text{As}_2 \) and \( \text{LaZnAsO} \). For \( \beta\text{-BaZn}_2\text{As}_2 \) and \( \text{LaZnAsO} \), we had expected that the common \([\text{ZnAs}]\) layers should form the bandgap both for the CBM and VBM. However, both the experimental and the calculation results show that the bandgap of \( \beta\text{-BaZn}_2\text{As}_2 \) is much smaller than that of \( \text{LaZnAsO} \). The similar difference in the bandgap is observed also in the Mn-based compounds (i.e. 0.14 eV for \( \text{BaMn}_2\text{P}_2 \),\(^{15,17} \) 1.7 eV for \( \text{LaMnPO} \),\(^{3} \) 0.06 eV for \( \text{BaMn}_2\text{As}_2 \),\(^{23,25,28} \) 1.5 eV for \( \text{LaMnAsO} \),\(^{3} \) 0.06 - 0.20 eV for \( \text{BaMn}_2\text{Sb}_2 \),\(^ {28} \) 1.0 eV for \( \text{LaMnSbO} \)). Here, we discuss the electronic structures of \( \beta\text{-BaZn}_2\text{As}_2 \) and \( \text{LaZnAsO} \), where we focus on the origins of the narrow bandgap in \( \beta\text{-BaZn}_2\text{As}_2 \).

The calculated total and projected densities of states (DOSs) for \( \beta\text{-BaZn}_2\text{As}_2 \) and \( \text{LaZnAsO} \) are shown in Figs. 3(a) and (b). The CB of \( \beta\text{-BaZn}_2\text{As}_2 \) between CBM and

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**Figure 1.** Crystal structures. Schematic illustrations for (a) \( \beta\text{-BaZn}_2\text{As}_2 \) (\( P4/mmm \)), (b) \( \text{LaZnAsO} \) (\( P4/mmm \)), and (c) trigonal \( \text{BaZn}_2\text{As}_2 \) (\( P-3m \), denoted as tri-\( \text{BaZn}_2\text{As}_2 \)). The \( d_{\text{as}} \) (equal to the lattice parameter \( a \)), \( d_{\text{out}} \) and \( d_{\text{inter}} \) parameters are defined as the distances between the nearest As neighbors along the in-plane, the out-of-plane and the interlayer directions, respectively, as denoted in (a). (c) Measured and simulated PXRD patterns for \( \beta\text{-BaZn}_2\text{As}_2 \) and \( \text{LaZnAsO} \) samples. (d) Comparison of coordination structures among \( \beta\text{-BaZn}_2\text{As}_2 \), \( \text{LaZnAsO} \), and tri-\( \text{BaZn}_2\text{As}_2 \), which plots the coordination number distribution of As atoms around an As atom as a function of As–As distance (\( d_{\text{as}}-\text{As} \)).

**Figure 2.** \( T \) dependence of \( \sigma \) for polycrystalline \( \beta\text{-BaZn}_2\text{As}_2 \) sample. The red curve is a fit to \( \sigma(T) = \sigma_0 \exp\left(-E_a/k_B T\right) + \sigma_{\text{vrh}} \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \).

We also calculated the bandgaps for \( \beta\text{-BaZn}_2\text{As}_2 \) and \( \text{LaZnAsO} \) by DFT calculations. First, we examined the PBE96 GGA functional, but it gave a negative bandgap for \( \beta\text{-BaZn}_2\text{As}_2 \) and an underestimated value of 0.56 eV for \( \text{LaZnAsO} \), which are consistent with the reported GGA results.\(^{4,25,28}\) It is caused by a well-known bandgap problem of DFT in which bandgaps are in general underestimated from experimental values. Then, we examined the HSE06 hybrid functional and found that it provided reasonable bandgaps of 0.23 eV for \( \beta\text{-BaZn}_2\text{As}_2 \) and 1.38 eV for \( \text{LaZnAsO} \), which are fairly close to the experimental values. Besides, HSE06 also gave better structural parameters than PBE96 (see Table S1 in Supporting Information).
CBM + 1.0 eV consists mainly of Ba 5d and As 4d hybridized with small portion of Zn 4s orbitals, which is highly dispersed as seen in the band structure in Fig. 3(c). The CB of LaZnAsO between CBM and CBM + 1.0 eV consists mainly of Zn 4s and As 4d orbitals with narrower dispersion as seen in Fig. 3(d). Both compounds exhibit long CB tails in the total DOSs near CBM. The origin of the CBM states will be discussed more definitely later on.

The VB of β-BaZnAs, consists mainly of As 4p orbital slightly hybridized with Zn 4p and Ba 5d orbitals; while that of LaZnAsO consists of As 4p orbitals slightly hybridized with Zn 4p orbitals in the shallow region (VBM to −3.6 eV), and the O 2p orbitals slightly hybridized with As 4p and La 5d orbitals in the deeper region (−3.6 to −6.0 eV). In particular, β-BaZnAs, exhibits a long tail structure in the total DOS from −0.6 eV to the VBM.

This characteristic structure is confirmed experimentally by HAXPES shown in Fig. 4(a). Fig. 4(b) magnifies the VB spectra around the VBM, which shows the different VB tail structures between β-BaZnAs, and LaZnAsO more clearly (note that the energy is measured from VBM and the respective Fermi levels are indicated by $E_F$ in the figure). LaZnAsO exhibits a linear VB edge just below the VBM along with tail states extending to the bandgap up to 0.2 eV above VBM. On the other hand, β-BaZnAs, exhibits two linear regions; one appears in the energy region deeper than 0.3 eV, and the other appears in the shallow region to VBM. Although similar tail structures are observed often in defective semiconductors such as amorphous In-Ga-Zn-O and also in the present LaZnAsO data, the calculated DOSs support the experimental data and the above interpretation; i.e., LaZnAsO has a single straight VBM structure while the VBM structure of β-BaZnAs, is curved as seen in the VB DOS in Fig. 4(c), guaranteeing that the upper linear tail region of Fig. 4(b) (0.35 eV in length) is not defect states but the intrinsic VB states. Besides, the $E_F$ of β-BaZnAs, and LaZnAsO were 0.04 eV and 0.34 eV above VBM, respectively, which are much lower than the half-bandgap levels, indicating these compounds are doped p-type semiconductors.

From the band structures in Figs. 3(c) and (d), we can see that the VB levels are split to four similar energy levels in β-BaZnAs, at the Z point, which is mainly explained by the intralayer hybridizations between the As atoms. The two bands marked by the red symbols are bonding (σ) and anti-bonding (σ*) orbitals of As 4p, respectively; while the other two by the blue symbols are bonding (π) and anti-bonding (π*) orbitals of As (4p, 4p,) orbitals, respectively, as confirmed from the decomposed DOSs of As 4p orbitals (the fifth panels of Figs. 3(a) and (b)). Each of them is doubly degenerated at the Z point, while splits to two bands along the $k$ vector moving to the Γ point because the adjacent [ZnAs] layers interact with each other and form a bonding and an anti-bonding states as indicated by σ$^*$ and σ$^*$ for example in Fig. 3(c). For LaZnAsO, the degenerated levels of As 4p at the Z point are the same as β-BaZnAs, while, each band does not exhibit a significant energy split along the Z − Γ direction (Fig. 3(d)), which is strikingly different from β-BaZnAs,.

Comparing the different VB structures, the most significant difference near the VBM is found in the σ$^*$ band of β-BaZnAs, formed due to the direct interlayer As 4p − As 4p, anti-bond (see Fig. 5(a)), which is highly dispersed and the maximum energy level exceeds the π$^*$ band by 0.36 eV at the Γ point; i.e., As 4p, mainly forms the lm-decomposed DOS of the shallow VB region as seen in the fifth panel of Fig. 3(b). This explains the tail structures observed in the total DOS and the HAXPES VB spectra (Fig. 4) for β-BaZnAs,.

The different VB dispersions are understood more clearly by the relative effective hole masses ($m_\text{h}/m_0$). The obtained $m_\text{h}/m_0$ values are 0.094 along Γ − Z and 0.88 along Γ − X for β-BaZnAs, which are much smaller than those of LaZnAsO (0.72 and 4.32, respectively). This result suggests that β-BaZnAs, should exhibit better hole transport along the c-axis than that in the a-b plane and also that β-BaZnAs, should exhibit much better hole transport than LaZnAsO.
Figure 3. (a and b) Total, projected, and $lm$-decomposed densities of states (DOS) of (a) $\beta$-BaZn$_2$As$_2$ and (b) LaZnAsO. The red and blue lines mark the valence band maximum (VBM) and the conduction band minimum (CBM), respectively. (c and d) Band structures of (c) $\beta$-BaZn$_2$As$_2$ and (d) LaZnAsO. The dashed lines mark the VBMs.

Figure 4. Valence band (VB) spectra of $\beta$-BaZn$_2$As$_2$ and LaZnAsO. (a) HAXPES VB spectra. (b) Magnified HAXPES VB spectra near VBM. (c) Calculated HSE06 DOSs. The binding energy ($E_b$) is aligned with respect to the VBM level ($E_v$).

**Origins of narrow bandgap of $\beta$-BaZn$_2$As$_2$: I: interlayer As–As hybridization.** As discussed above, the $\Gamma$ point splitting of the VB in $\beta$-BaZn$_2$As$_2$ (denoted as secondary splitting hereafter) is caused by the direct hybridization between interlayer As atoms (schematically shown in Fig. 5(a)) due to the relatively short $d_{\text{inter}}$ (0.370 nm). To further confirm this model, we performed HSE06 calculations for several hypothetical structures of $\beta$-BaZn$_2$As$_2$, with fixed [ZnAs] layers and varied $d_{\text{inter}}$ values, as illustrated in Fig. 5(a). The obtained bandgap vs. $d_{\text{inter}}$ relation is summarized in Fig. 5(b), and those band structures and DOSs are shown in Figs. 5(c) and (d), respectively. First, we slightly decreased the $d_{\text{inter}}$ from 0.370 to 0.360 nm. The secondary splitting of As $4p$ became wider because of the larger hybridization of the interlayer As atoms, which raised the VBM energy level as shown in the left panel in Fig. 5(c). As a result, the bandgap value is decreased to 0.04 eV. When the $d_{\text{inter}}$ was increased to 0.380 nm, the secondary splitting of As $4p$ became smaller due to the reduced interlayer hybridizations, which led to a lowered VBM and an increased bandgap of 0.40 eV. By further increasing the $d_{\text{inter}}$ to 0.400 nm, the secondary splitting became further smaller and the $\sigma'$ band did not pass across the $\pi'$ band anymore (the right panel of Fig. 5(c)), which made the VB structure more similar to that of LaZnAsO. Correspondingly, the “tail” structure near VBM faded away completely as seen in Fig. 5(d). The resulted bandgap was further increased to 0.66 eV. We confirmed that further increasing $d_{\text{inter}}$ did not increase the bandgap significantly. From the $d_{\text{inter}}$ dependence of bandgap summarized in Fig. 5(b), we can conclude that the interlayer hybridization between the As $4p_z$ orbitals of adjacent layers is an origin of the narrow bandgap in $\beta$-BaZn$_2$As$_2$, which decreases the bandgap by ~0.43 eV (the bandgap difference between the actual structure ($d_{\text{inter}} = 0.370$ nm) and that with $d_{\text{inter}}$ being 0.400 nm) here. Here, we should note that the $d_{\text{inter}}$ value in $\beta$-BaZn$_2$As$_2$ is shorter than that in LaZnAsO, but much longer than As–As bonds in single-bonded As$_2$-dimers (0.240 – 0.260 nm)\(^\text{30}\) in such as CaNi$_2$As$_2$.\(^\text{30}\) This means that the interlayer hybridization of the As $4p_z$ orbitals in $\beta$-BaZn$_2$As$_2$ is much weaker than the As$_2$-dimers and is of an intermediate case.

**Origins of narrow bandgap of $\beta$-BaZn$_2$As$_2$: II: non-bonding Ba 5d$_{\alpha-\gamma}$ orbital.** As discussed above for the PDOS in Fig. 3(a), the Ba 5$d$ orbitals contribute largely to the CB, in particular to the CBM structure. To examine the role of the Ba 5$d$ orbitals on the narrow bandgap, we further calculated $lm$-decomposed DOSs for the five Ba 5$d$ orbitals (i.e. $d_{\alpha}$, $d_{\beta}$, $d_{\gamma}$, $d_{\alpha-\beta}$ and $d_{\alpha-\gamma}$) as shown in the rightmost panel of Fig. 3(a). It is known well that the energy levels of outer $d$ orbitals are split by the coordinating ligands, whose energy splits are understood qualitatively from the ligand symmetry ($D_{\text{hyb}}$ around Ba, as shown in Fig. 6(a)) by the group theory. The energy level of the edges of Ba 5$d$ orbitals derived from the ligand theory and the $lm$-decomposed DOSs is schematically shown in Fig. 6(c). As known from the $lm$-decomposed DOSs, the $d_{\alpha-\gamma}$ has the lowest energy among the five $d$ orbitals, and is even lower than that of Zn 4$s$ orbital (the dashed line in Fig. 6(c)), and forms the CBM. As drawn in Fig. 6(a), the $d_{\alpha-\gamma}$ wave function extends to the interstitial spaces between the neighboring As $4p$ orbitals, minimizes the charge overlap with the As electrons, lowers its energy level due to the small Coulomb repulsion, and forms the deep CBM. Further, as the Ba 5$d_{\alpha-\gamma}$ – As $4p$ states are non-bonding states due to the point-group symmetry and the restriction of the translational symmetry at the Ba site,
which diminishes the energy upshift due to the anti-bonding interaction between the Ba 5d_{ε,γ} and As 4p orbitals and also contributes to the formation of the deep CBM. This is similar to the case of superdegeneration observed e.g. in cubic perovskites; for example, the bandgaps of GeO_{3} are >6 eV, but that in cubic SrGeO_{3} is reduced to 2.7 eV due to the non-bonding nature of Ge 4s.

In contrast, LaZnAsO has a lower ligand symmetry of C_{s} around La (see Fig. 6(b)), and each La 5d orbital cannot avoid hybridization with O 2p and As 4p orbitals, where anti-bonding interaction raises the CBM. The energy split of La 5d orbitals is much narrower, as seen from the \( lm \)-decomposed DOSs in the rightmost panel of Fig. 3(b) and the derived schematic energy diagram in Fig. 6(d). Besides, the energy levels of La 5d orbitals are also up-shifted significantly and are higher than the Zn 4s level due to the anti-bonding interaction between the La 5d and the O 2p and As 4p orbitals. As a result, La 5d orbitals do not contribute to the CBM structure, and the bandgap is mainly formed in the [ZnAs] layer (note that the bandgap of a single [ZnAs] layer is 1.48 eV. See Fig. S1 in Supporting Information). From the above discussion, we conclude that the non-bonding Ba 5d_{ε,γ} orbital forms the deep CBM and contributes to the narrow bandgap of \( \beta \)-BaZn_{2}As_{2}.

![Figure 6](image)

**Figure 6.** (a,b) Ligand geometries of (a) \( D_{3h} \) around Ba in \( \beta \)-BaZn_{2}As_{2} and (b) \( C_{s} \) around La in LaZnAsO. The wave functions of the As 4p orbitals, the O 2p orbitals and the lowest 5d orbitals of Ba and La are also shown schematically. (c,d) Schematic energy diagrams near the VBM and the CBM for (c) \( \beta \)-BaZn_{2}As_{2} and (d) LaZnAsO. The energy levels are derived from the \( lm \)-decomposed DOSs in Figs. 3(a,b) and aligned by Zn 3d levels.

**Large bandgaps in trigonal 122-type pnictide semiconductors.** From the above discussion, we concluded that the two origins (the direct hybridization between the interlayer As atoms and the nonbonding state of Ba 5d_{ε,γ}) cause the narrow bandgap in 122-type pnictides due to the local \( D_{3h} \) symmetry. The latter origin suggests that the energy level of Ba 5d is affected largely by the ligand field and the local symmetry; i.e., lower local symmetry would raise the Ba 5d levels and widen the bandgap of 122-type compounds.

Here, we examined the electronic structure of a hypothetical trigonal BaZn_{2}As (Fig. 1(c), denoted as tri-BaZn_{2}As, hereafter) because a trigonal 122-type structure with \( D_{3h} \) local symmetry (space group P-3m1) has been reported for \( \text{AeT}_{m} \text{Ps}_{n} \). Due to the trigonal symmetry in tri-BaZn_{2}As, each [ZnAs] tetrahedron connects with 3 neighboring [ZnAs] tetrahedra by sharing their edges, which is different from the tetragonal \( \beta \)-BaZn_{2}As and LaZnAsO (4 neighboring [ZnAs] tetrahedra). Compared with \( \beta \)-BaZn_{2}As, the tri-BaZn_{2}As has similar intralayer As––As distances (i.e., \( d_{intra} \) and \( d_{inter} \)) but a much larger interlayer As––As distance (\( d_{inter} = 0.494 \) nm) as shown in Fig. 1(e).

The calculated DOSs and band structure are shown in Figs. 7(a) and (b), respectively. Just as expected, the bandgap of tri-BaZn_{2}As is increased significantly to 0.92 eV. This bandgap increase is understandable based on the above discussion. The As 4p orbitals do not exhibit the secondary splitting and do not raise the VBM unlikely observed in \( \beta \)-BaZn_{2}As (see Fig. 7(b)) due to the large \( d_{inter} \) value. On the other hand, due to the \( D_{3h} \) symmetry around the Ba atoms, all the five Ba 5d orbitals hybridize with As 4p orbitals (seen in Fig. 7(c)) and have almost the similar energy levels, as can be seen in the \( lm \)-decomposed DOSs in the rightmost panel of Fig. 7(a) and as summarized in the energy diagram in Fig. 7(d). Consequently, the energy levels of Ba 5d orbitals are pushed up to a higher energy than Zn 4s so that the CBM mainly consist of Zn 4s orbitals hybridized with Ba 5d and As 4d orbitals.

We further examined tri-SrZn_{2}As_{2} and tri-CaZn_{2}As_{2}, and found that they have similar electronic structures as that of tri-BaZn_{2}As (see Fig. S2 in Supporting Information). Their total energies (Fig. 7(e)) are consistent with experimental results; i.e., the tri-BaZn_{2}As structure has a higher energy than the tetragonal \( \beta \)-BaZn_{2}As, while the trigonal structures are more stable for SrZn_{2}As_{2} and CaZn_{2}As_{2}. The calculated bandgaps are 1.12 and 1.27 eV, respectively. The order of the bandgap increase from tri-BaZn_{2}As to tri-SrZn_{2}As_{2} and finally to tri-CaZn_{2}As_{2} can be understood from the increase in the energy levels of the outer d orbitals from Ba to Ca. This result indicates that the difference in the d energy levels is 0.35 eV among Ba, Sr, and Ca in the trigonal structures.

We also calculated the \( m_{b}/m_{o} \) from the VBM band dispersions. The \( m_{b}/m_{o} \) values are 0.522 along the \( \Gamma \rightarrow Z \) and 0.486 along the \( \Gamma \rightarrow X \) for tri-SrZn_{2}As_{2}, and 0.508 along the \( \Gamma \rightarrow Z \) and 0.551 along the \( \Gamma \rightarrow X \) for tri-CaZn_{2}As_{2}. These small \( m_{b}/m_{o} \) values suggest that tri-BaZn_{2}As to tri-CaZn_{2}As_{2} could be good \( p \)-type semiconductors with high hole mobilities.
flexible control of bandgap and carrier transport in versatile pnictide compounds.

ASSOCIATED CONTENT

Supporting Information

Literature and calculated lattice parameters, electronic structures of a single [ZnAs] layer, tri-CaZnAs, and tri-CaZnAs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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