

¹X. enZ an, ²A. J. Feeh an, ¹ and Ae Z n e ²
1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 6020,

= A, Ga, In, Sc, Y, and La), p c b c A

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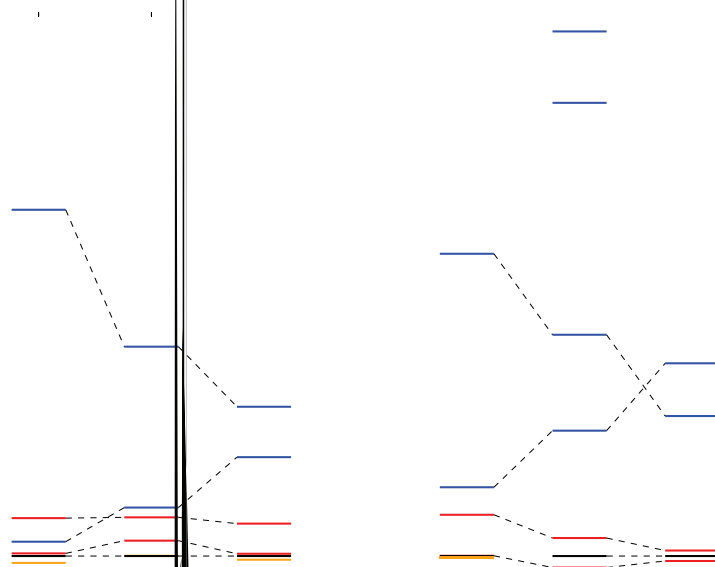


FIG. 1. Energy band structure.

STRUCTURALLY UNSTABLE $A^{III}BiO_3$

Perovskite structures where the octahedra are allowed to tilt: relative stability of the two $Pnma$ $GdFeO_3$ -type perovskite variants. A whole range of distorted perovskite structure types can be obtained starting from the ideal cubic perovskite by octahedra rotations and cation shifts. These distorted structures can lower the energy by optimizing the atom packing. The $Pnma$ $GdFeO_3$ structure-type in particular is the perovskite in which the octahedra can tilt around a generic axis and distort from the ideal regular shape. As shown in Fig. 1, the energy of the $A^{III}BiO_3$ compounds decreases considerably going from the $Pm\bar{3}m$ to the $Pnma$ perovskite structure, regardless of the Bi position. The configuration with Bi at the cavity site is still energetically preferred, but with an energy distance from the configuration with Bi at the $10d$ site much reduced with respect to the $Pm\bar{3}m$ perovskite and as low as 0.1 eV/at. Moreover, the $GdFeO_3$ -type structure with the A^{III} cation at the octahedral site, is close in energy to the experimentally observed structure of $AlBiO_3$ and $InBiO_3$ and degenerate with this in the case of $ScBiO_3$.

Electronic structure of the $GdFeO_3$ -type perovskites. The $A^{III}BiO_3$ systems in the $Pnma$ perovskite structure are insulators but without the s - p band inversion observed in the $Pm\bar{3}m$ form. Figure 3 compares the GGA+SOC band structure of $InBiO_3$ in the $Pm\bar{3}m$ and $Pnma$ perovskite structures with Bi at the octahedral site. While $InBiO_3$ in the $Pm\bar{3}m$ structure is a metal with the s - p band inversion at the R point at about 3 eV above the Fermi level, the octahedral tilting and internal distortions that produce the $GdFeO_3$ -type structure open a band gap but remove the inversion. We find that all $A^{III}BiO_3$ systems in this $Pnma$ perovskite are trivial insulators with $Z_2 = 0$ irrespective of the Bi position.

GSGO-predicted and experimental structures.

position, metallic or trivial insulators in the cubic perovskite structure which is, however, unstable. When the octahedra are allowed to tilt, the cubic perovskite relaxes into distorted perovskite phases of much lower energy. However, we find