Tuning the gap of lead-based halide perovskites by introducing superalkali species at the cationic sites of ABX$_3$-type structure

C. Paduani and Andrew M. Rappe

We study with scalar relativistic density functional theory (DFT) calculations the effect of changes in the ionicity of the bonding mechanism and charge donation on the structure and electronic properties of new lead halide perovskites which show promising performance in optoelectronic applications as long-wave infrared detectors and thermoelectrics. Our results provide evidence that the band gap of these compounds can be tuned upon the introduction of appropriate superalkali moieties at the cationic A-sites in the CsPbI$_3$-type structure. The computed band gap is 0.36 eV (direct) and 0.41 eV (indirect) for [Li$_2$O]PbI$_3$ and [Li$_2$S]PbI$_3$, respectively. By changing the chemical environment in the Pb-halide perovskite structure, we see drastic changes in the shape of both valence and conduction bands, as compared to CsPbI$_3$. Introducing superalkali cations produces extra electronic states close to the Fermi level which arise from the formation of delocalized energy states, where a strong hybridization is identified between Pb and Li s-states near the top of the valence band. This can promote the hole mobility and increase the exciton diffusion length at longer wavelengths. Berry phase calculations show rather significant spontaneous polarization of 34 and 15 μC cm$^{-2}$ along the x-axis in both [Li$_2$O]PbI$_3$ and [Li$_2$S]PbI$_3$, indicative of ferroelectric behavior.

Introduction

Despite the fact that perovskites with ABX$_3$ structure have long been studied, only recently have these compounds been considered as the most promising candidates for applications in photovoltaics and other optoelectronic devices. The recent interest in photovoltaic materials has been piqued with the advent of the organic–inorganic hybrid perovskites (OIHPs), which are low-cost emitters with very high color purity. The OIHPs attract even greater focus because of their easy solution-based synthesis, high conversion efficiency, and outstanding photovoltaic performance in photovoltaic applications as long-wave infrared detectors and thermoelectrics. Our results provide evidence that the band gap of these compounds can be tuned upon the introduction of appropriate superalkali moieties at the cationic A-sites in the CsPbI$_3$-type structure. The computed band gap is 0.36 eV (direct) and 0.41 eV (indirect) for [Li$_2$O]PbI$_3$ and [Li$_2$S]PbI$_3$, respectively. By changing the chemical environment in the Pb-halide perovskite structure, we see drastic changes in the shape of both valence and conduction bands, as compared to CsPbI$_3$. Introducing superalkali cations produces extra electronic states close to the Fermi level which arise from the formation of delocalized energy states, where a strong hybridization is identified between Pb and Li s-states near the top of the valence band. This can promote the hole mobility and increase the exciton diffusion length at longer wavelengths. Berry phase calculations show rather significant spontaneous polarization of 34 and 15 μC cm$^{-2}$ along the x-axis in both [Li$_2$O]PbI$_3$ and [Li$_2$S]PbI$_3$, indicative of ferroelectric behavior.

The hybrid organic lead halide with the methylammonium (MA) molecular cation CH$_3$NH$_3^+$ in MAPbX$_3$ has attracted a particularly great deal of attention from researchers because, allied to its relatively low cost, it possesses remarkable solar-cell efficiency in photovoltaic applications, besides being an efficient ionic conductor. It exhibits pronounced piezoelectricity due to a weak bonding interaction and rotation of the MA molecules, which have a permanent dipole due to the charge imbalance between the methyl radical and the ammoniumyl radical. The piezoelectric effect of MAPbI$_3$ has been attributed to the dipole reorientation. However, the role of the MA molecule includes not only its own dipole and off-center displacement, but also the transverse shift between the Pb and I atoms. The latter enhances the separation between the positive (i.e., Pb atoms) and negative charge centers (i.e., I atoms) inside the Pb$_6$ octahedra, providing another contribution to the piezoelectric response of MAPbI$_3$. The ionic disorder actually has been considered to be more significant than electronic disorder in this material. However, the major drawback to its widespread use is its inherent instability and degradation upon exposure to oxygen or water. It has been shown that point defects

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(involving Pb, I or MA) lead to shallow traps near the valence and conduction band edges which may provide unintentional p- or n-type doping, and therefore organic components other than MA will contribute to trap states. The size and charge of the molecule that occupies the perovskite A sites will obviously influence the energy barrier for ionic transport, in addition to the fact that the size of the organic molecule is also essential for stabilizing the perovskite structure. Recent studies using a multi-scale approach for a comprehensive investigation over several materials have been undertaken as an effort to identify the key parameters and mechanisms that control the basic properties and the stability of HPs.\textsuperscript{12,13}

Results of cluster calculations\textsuperscript{21–28} mimicking the alkali halides in several materials have shown that it is possible to get quick estimations for the properties of new compounds on the basis of simple molecular models. It has been verified that the structures of organic SAs indeed remain practically constant in all materials and hardly change from their geometries in the gas phase. Here, we demonstrate that by changing the building blocks from atomic ions to super-ions, we can create HPs with unusual properties, with the basic properties of these materials largely determined by the ionic radii and the bonding ionicity of the super-ions occupying the cationic sites. Several strategies have been proposed to counter the degradation by moisture: the lowering of the binding energy between the water molecule and the SA halide (in order that the water molecule does not get trapped between the ions easily), the enhancement of the bonding between the M and X units within the MX\textsubscript{3} structure (so that the water molecules cannot easily remove any of the X atoms from the octahedra), and the replacement of the organic cations of the HPs with inorganic cations having comparably large size and proper electronegativity.

Another recent example of perovskite tunability is the rapidly growing family of layered perovskites, which has attracted considerable attention due to unique crystal structures and optoelectronic properties. Recently a solution-based cation infiltration process has been developed to deposit layered perovskite structures onto methylammonium lead iodide films to produce a perovskite/perovskite heterojunction solar cell.\textsuperscript{29} By partially substituting small methylammonium cations for bulkier ones, the resulting compound resembles a multi-quantum well structure.\textsuperscript{30} These have been studied in a previous work,\textsuperscript{31} and have also been experimentally obtained.\textsuperscript{32,33} In this study, these clusters were initially placed at the corners of the unit cell in several inequivalent orientations. The calculations for the geometry optimization are thus performed starting from a simple cubic supercell but however considering a variable cell during the relaxation procedure along the x, y, z directions. We want to stress that, in order to assure that the obtained equilibrium geometries are indeed the ground-state structures, the relaxation process was performed from several different starting configurations. The plane wave cutoff was taken at 78 Ry. All geometries were fully relaxed, and thresholds for convergence of the total energy and forces were set to $1 \times 10^{-6}$ eV per cell and $1 \times 10^{-2}$ eV Å\textsuperscript{-1}, respectively. Crystal structures are visualized using the XCrysden program suite.\textsuperscript{34}

Results and discussion

Examples of SA are Li\textsubscript{2}F, Li\textsubscript{2}O, Na\textsubscript{2}O, Li\textsubscript{3}S, and Li\textsubscript{3}N. In Fig. 1, we show the equilibrium geometries of the SA clusters Li\textsubscript{2}O and Li\textsubscript{3}S. These have been studied in a previous work,\textsuperscript{37} and have also been experimentally obtained.\textsuperscript{38,39} In this study, these clusters are inserted at the cationic A-sites, replacing the Cs atoms in the CsPbI\textsubscript{3} material. The final crystal unit cell geometry was obtained by fully relaxing the unit cell. Initially, we performed extensive calculations in supercells built up by stacking two unit cells along all three orthogonal directions. We have tried several different tiltings and rotations of the PbI\textsubscript{6} octahedra, as well as six different orientations of the SA clusters in the structure, in order to find the lowest-energy equilibrium geometry. A volume relaxation of the initially cubic parent phase resulted in equilibrium geometries which exhibit small tetragonal distortions for both Li\textsubscript{2}OPbI\textsubscript{3} and [Li\textsubscript{3}S]PbI\textsubscript{3} (see Table 1). For cubic CsPbI\textsubscript{3}, $a = 6.2894$ Å.\textsuperscript{40} It is interesting to note that the structures of both Li\textsubscript{2}O and Li\textsubscript{3}S at the cationic A-sites are essentially preserved in the equilibrium geometries of the perovskites [Li\textsubscript{3}O]PbI\textsubscript{3}.
we see the PbI$_6$ cage slightly bent in the R

band gap close to A-cation,

factors: anion. The perovskite structure is favored by the following tolerance tetragonal structures. In the present study, perovskites, a

perovskites, 0.41 eV, for [Li$_3$O]PbI$_3$ and [Li$_3$S]PbI$_3$, respectively (see Table 1).

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The Goldschmidt tolerance factor (z) is a dimensionless number which is an indicator for the stability and distortion of crystal structures, originally only used to describe the perovskite structure; $z \equiv (r_A + r_X)/[\sqrt{2}(r_A + r_X)]$, where $r_A$ is the ionic radius of the A-cation, $r_X$ is the radius of the B-cation, and $r_X$ is the radius of the anion. The perovskite structure is favored by the following tolerance factors: $z = 0.90–1.0$ for cubic perovskites, $z = 0.80–0.89$ for distorted perovskites, $z < 0.80$ for other types and $z > 1.00$ for hexagonal or tetragonal structures. In the present study, $z = 0.97$ for [Li$_3$O]PbI$_3$ and 1.07 for [Li$_3$S]PbI$_3$, suggesting that they are viable alternatives for polyatomic cations in stable perovskites.

The calculated band structure of these perovskites at high-symmetry points of the Brillouin zone are presented in Fig. 2 (the Fermi energy is shifted to zero). Observe that in [Li$_3$O]PbI$_3$ the valence band maximum and conduction band minima occur exactly at the R point, whereas in [Li$_3$S]PbI$_3$ we see an indirect band gap close to R. Within 1 eV below the Fermi energy $E_F$ one sees flattened bands, a feature even more pronounced for [Li$_3$O]PbI$_3$. The remarkable result is that the band gap is 0.36 eV and 0.41 eV, for [Li$_3$O]PbI$_3$ and [Li$_3$S]PbI$_3$, respectively (see Table 1). The experimental results for the band gap for CsPbI$_3$ and MAPbI$_3$ are 3.14$^{11}$ and 1.5 eV, respectively.

Table 1 Calculated parameters for the lead halide perovskites

<table>
<thead>
<tr>
<th></th>
<th>Lattice constants (Å)</th>
<th>Cell volume (Å$^3$)</th>
<th>Electric polarization (µC cm$^{-2}$)</th>
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<td>[Li$_3$O]PbI$_3$</td>
<td>6.93</td>
<td>6.88</td>
<td>6.99</td>
<td>333.27</td>
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<tr>
<td>[Li$_3$S]PbI$_3$</td>
<td>6.62</td>
<td>6.61</td>
<td>6.51</td>
<td>284.86</td>
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Fig. 2 Band structure along symmetry directions for (a) [Li$_3$O]PbI$_3$ and (b) [Li$_3$S]PbI$_3$.

The calculated densities of states (DOS) are depicted in Fig. 3. The uppermost part of the valence band spreads out over $-4$ to 0 eV. From these diagrams we see clearly that, in the energy range $-2$ to 0 eV, the major contributions to the total DOS of [Li$_3$O]PbI$_3$ arise from O 2p states, whereas in the range $-4$ to 2 eV these are derived from I 5p states. Correlating these DOS results with Fig. 2, we identify the dominant contributions to the bands in these energy ranges as arising from O and I p states. Above $E_F$, the Pb 6p states are dominant. Similarly, for [Li$_3$S]PbI$_3$ we can see overwhelming contribution arising from S 3p states in the energy range $-1$ to 0 eV, while the I p states are responsible for the main contribution to the total DOS in the range $-4$ to 2 eV. Furthermore, we observe in both cases that the predominant contribution to the s DOS right below $E_F$ comes from the Li atoms, which are seen to be strongly hybridized with the Pb s states. Just above $E_F$, the s states are mostly I s-states, which are also seen to be strongly hybridized with the Pb p states. As a common feature in these compounds, we observe that, close to the Fermi energy, the valence bands are governed by I and O/S p states, whereas above $E_F$ the Pb p states dominate the lowest conduction bands.

Ferroelectric materials are characterized by spontaneous electric polarization that is lost as the material is heated above $T_C$. The permanent dipole associated with the molecular cations in OIHs may lead to spontaneous polarization and thus ferroelectricity and piezoelectricity. The application of ferroelectric materials in solar cells has long been considered, from the first observations of the anomalous photovoltaic effect and the bulk photovoltaic effect until the recent successful application of OIHs in solar cells emphasizing that polar semiconductors indeed can be used in conventional photovoltaic architectures. Theoretical studies have estimated the value of the polarization density for the ferroelectric phase of MAPbI$_3$ at room temperature to be of the order of a few µC cm$^{-2}$. Polarization is induced by the rotation of the methylammonium ions inside the PbI$_6$ cages. A recent study shows that the piezoelectric coefficient depends sensitively on the molecular ordering. By comparing organometallic halide perovskites with different atomic substitutions, it has been observed that the displacement of the B-site cation contributes to the piezoelectric response as well as the competition between A-X hydrogen bonds and B-X...
metal–halide bonds. According to the modern theory of polarization,\textsuperscript{46} the spontaneous polarization of a ferroelectric crystal or the macroscopic polarization of a crystalline dielectric can be calculated as a Berry’s phase of the electronic Bloch wavefunctions. We performed Berry’s phase calculations to find the electric polarization. The components of the polarization vectors are listed in Table 1. For [Li₃O]PbI₃, one can see a rather significant polarization in the xy-plane, with the larger component along the x direction (34 \( \mu \)C cm\(^{-2} \)). For [Li₃S]PbI₃, we see also a similar in-plane polarization, with largest component of 15 \( \mu \)C cm\(^{-2} \), also along the x direction.

We also performed a Löwdin population analysis in order to determine partial atomic charges in these compounds. For [Li₃O]PbI₃, the valence electronic charges assigned to the Li, O, Pb and I atoms are 0.27 e, 7.00 e, 3.41 e, and 7.32 e (average), respectively, which imply net charges of +0.73 e, −1.00 e, +0.59 e, and −0.32 e, respectively. The Li–O bonding thus remains primarily ionic in these perovskites. For [Li₃S]PbI₃, the valence electronic charges assigned to the Li, S, Pb and I atoms are 0.35 e, 6.93 e, 3.43 e, and 7.29 e, which suggest net charges of +0.65 e, −0.93 e, +0.57 e, and −0.29 e, respectively. In [Li₃O]PbI₃, the net charge on the SA cluster is thus +1.19 e, whereas in [Li₃S]PbI₃ it is +1.02 e. From our previous study,\textsuperscript{37} the vertical ionization potentials (VIPs) for Li₃O and Li₃S are 3.86 eV and 4.52 eV, respectively. The lower VIP of [Li₃O]PbI₃ directly leads to its larger donation of charge as an A-site cation. The net

Fig. 3 Projected densities of states for [Li₃O]PbI₃ (left) and [Li₃S]PbI₃ (right).
charge in the PbI₃ cage in this perovskite is $-0.37 \, e$, whereas in [Li₃S]PbI₃ this is $-0.30 \, e$.

Despite the greater charge transfer in [Li₃O]PbI₃, its unit cell volume is larger by $\approx 14\%$. This is due to the larger dimensions of the planar trigonal Li₃O cation as compared with the pyramidal Li₃S (Fig. 1). This translates into larger PbI₃ cages in [Li₃O]PbI₃, where the Pb-I bond lengths are larger (3.47 Å) than in [Li₃S]PbI₃ (3.38 Å). We therefore observe that, in these materials, the polarization is due to a combined effect of moderately-enhanced effective ionic charges in addition to the alignment of the polar SA moieties. The primarily ionic character of the bonding mechanism and the asymmetric orientations of the polyatomic ions in the structure lead to tetragonal distortion, and thereby lack of inversion symmetry (noncentrosymmetry) of these compounds.

As shown in Fig. 2, the introduction of the SA clusters Li₃O and Li₃S replacing the Cs atoms in CsPbI₃ leads to the formation of new bands in the energy range $-2 \rightarrow 0$ eV in both [Li₃O]PbI₃ and [Li₃S]PbI₃ compounds, as compared to CsPbI₃.⁴⁷ Within 1 eV below the valence band edge, these are ascribed to the O and S p states, and as a common feature we see strong hybridization with the Li 2s states. In addition, we see tendency for the formation of flattened bands below $-2 \, eV$. In the conduction band, we see accumulation of bands around the $R$ point in both [Li₃O]PbI₃ and [Li₃S]PbI₃. From a close inspection of the shape of the band plots in Fig. 2 we can see that the introduction of SA species replacing Cs atoms promotes the carrier mobility and increases the exciton diffusion length at longer wavelengths, relatively to CsPbI₃. Moreover, there is a remarkable decrease of the computed band gap in these new materials (0.36 eV and 0.41 eV), as compared to CsPbI₃ (2.27 eV).⁴⁷

The accumulation of bands close to $E_F$ is even more pronounced in [Li₃S]PbI₃ (see Fig. 2b), which has a stronger hybridization between Pb and Li s states. Furthermore, a distinctive feature for these new compounds is the combination of the two peaks in the [Li₃O]PbI₃ DOS below $E_F$ into a prominent broader peak at about $-0.5 \, eV$ for [Li₃S]PbI₃, as one replaces S for O. The change in the donation of bonding charge which arises from the SA substitution for the Cs atoms affects drastically the band structure of the virtual bound states (above $E_F$) in both [Li₃O]PbI₃ and [Li₃S]PbI₃, and therefore we see a shift upwards of the conduction band for I s- and Pb p-states, which is particularly seen even more pronounced at the $R$-point in [Li₃S]PbI₃.

We performed test cluster calculations with the Gaussian-09 package⁴⁸ at the B3LYP/6-311+G(2df) level of theory in order to study the structure and stability of clusters formed by the SA species Li₃O or Li₃S in the presence of a water molecule. In Fig. 4 we show HOMO (highest occupied molecular orbital) plots and natural atomic orbital (NAO) occupancies computed by the population analysis. The Li₃O cluster keeps its structural integrity after the addition of the water molecule, despite some changes in the NAO charges on the Li and O atoms. Note that both Li₃O and H₂O are neutral. On the other hand, the Li₃S cluster is significantly distorted and is disrupted upon the addition of the H₂O molecule. One H atom strongly bonds with the S atom, whereas the OH radical attracts two Li atoms, giving an Li₃OH moiety with a net charge of $+0.38 \, e$. The characteristics of the bonding mechanism are depicted in the HOMO plots, where we can see much weaker bonding at the HOMO level for Li₃O/H₂O. These features are indicative of less moisture sensitivity for this cluster. The dissociation energies of the Li₃O and Li₃S clusters have been calculated in a previous work:⁴⁷ 2.1 eV and 1.5 eV, respectively. These give an estimate of their thermodynamic stability relatively to decomposition into plausible small fragments. The significant calculated values indicate good stability for these clusters.

Furthermore, in order to get more insight on the stability of these compounds, we performed also cluster calculations at the B3LYP/SDD/6-311+G(2df) level to study the enthalpy change $\Delta H$ (internal energy/per atom) for fragmentation along selected channels. The clusters adopted to represent the solid phases are built up with the same geometry (when available) of the solid phases where all dimensions are accurately preserved. For LiOPbI₃ and LiSPbI₃ we performed geometry optimization procedure. We run also frequency calculations in order to check for imaginary frequencies, which indeed do not occur. In Table 2 we can see that the largest $\Delta H$ ($-0.72 \, eV$) for [Li₃O]PbI₃ is seen along the decomposition channel Li₃OPbI₃ $\rightarrow$ LiOPbI₃ + 2Li. On the other hand, for [Li₃S]PbI₃ we see that the largest $\Delta H$ ($-0.60 \, eV$) takes place along the reaction Li₃SPbI₃ $\rightarrow$ LiSPbI₃ + 2Li. These results show that both [Li₃O]PbI₃ and [Li₃S]PbI₃ systems are somewhat unstable. However, the results of the frequency calculations with all vibrational modes having positive frequency suggest that these hypothetical structures are moderately unstable and at least locally stable (metastable). In addition, we performed also DFT calculations of the vibrational frequencies (normal modes/phonons) with Quantum ESPRESSO. The calculated Raman spectra for our compounds are showed in Fig. 5. The infrared (IR) spectra are very weak, as one should expect for these noncentrosymmetric systems which have missing inversion symmetry. For a molecule with a center of symmetry, vibrations which are infra-red active are Raman forbidden, and vice versa.
is expected for \([\text{Li}_3\text{O}]\text{PbI}_3\), which present smaller number of low-stability. Besides, these results also indicate that a larger stability of negative frequencies, are thus indicating thermodynamic associated with higher frequencies, which, allied to the absence have very low amplitudes. The stronger resonances are asso-
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Fig. 5 Calculated Raman spectra.

There can also be vibrations forbidden in both, but none allowed in both effects. In the present study, the obtained results show normal modes for weaker bands at the low-frequency side of the spectrum for both materials. They get rapidly stronger as the displacement gets larger for the stretch- ing modes, thus indicating strong absorption. In the Raman plots of Fig. 5, for both compounds, we see that the low-frequency modes, which are indicative of inherent instability, have very low amplitudes. The stronger resonances are associated with higher frequencies, which, allied to the absence of negative frequencies, are thus indicating thermodynamic stability. Besides, these results also indicate that a larger stability is expected for \([\text{Li}_3\text{O}]\text{PbI}_3\), which present smaller number of low-frequency modes.

It is noteworthy to mention that, according to the Laporte rule, in a centrosymmetric environment, electronic transitions that conserve parity between like atomic orbitals such as s–s, p–p, d–d, or f–f transitions are forbidden. Actually, most forbidden transitions are only relatively unlikely, and although electric dipole transitions can be nominally forbidden, there is a small probability of their spontaneous occurrence. Dipole-forbidden transitions between energy levels may also occur based on other mechanisms such as quadrupole transitions. In the present study, we show that the SA substitution introduce drastic changes in the shapes of both valence and conduction bands, comparatively to \(\text{CsPbI}_3\), and gives rise to the onset of extra energy states close to \(E_g\). The formation of delocalized energy states is favored through a strong hybridization between Pb and Li s-states, in addition to the s–p hybridization, near the top of the valence band. Hence, despite the overwhelming contribution of p-orbitals close to the Fermi energy, the reduced symmetry in this noncentrosymmetric environment allows the valence orbitals to mix and hybrids to form, the lobes of which point along the bonding directions. The so formed bonding molecular orbitals have symmetry characteristics in common with respect to the axis of the bond. The resulting breaking of symmetry is thus a determining factor for allowing optical transitions which are parity forbidden. Nevertheless, one expects that the p–p transition is disallowed by the symmetry rule when both p orbitals are on the same atom. Finally, the results above show that the introduction of SA species at the cationic A-sites in the \(\text{CsPbI}_3\)-type structure of lead-based halide perovskites is favorable for reducing the band gap and thereby extending optical absorption and photovoltaic response to long wavelength radiation. These features are expected to contribute to the lowering of the effective mass of holes, improving the hole mobility and increasing exciton diffusion length. We hope this study will stimulate further experimental investigations to exploit new possibilities for synthesizing novel structures.

### Conclusions

We investigate the structure and electronic properties of new lead-based halide perovskites formed by introducing the SA clusters \(\text{Li}_3\text{O}\) and \(\text{Li}_3\text{S}\) in place of the Cs atoms in the cubic structure of \(\text{CsPbI}_3\). The results show that the equilibrium crystal structures of both \([\text{Li}_3\text{O}]\text{PbI}_3\) and \([\text{Li}_3\text{S}]\text{PbI}_3\) are slightly tetragonally distorted. A remarkable result is that the band gaps in both systems are much smaller than that of cubic \(\text{CsPbI}_3\). The smaller gaps arise from the strong hybridization between Li and Pb s-states at the top of the valence band. The band gap is slightly larger in \([\text{Li}_3\text{S}]\text{PbI}_3\) because there occurs a shift of both conduction and valence states towards higher energies, relatively to \([\text{Li}_3\text{O}]\text{PbI}_3\). Cluster calculations indicate that the \([\text{Li}_3\text{O}]\text{PbI}_3\) compound is expected to be more resistant to water exposure. The present results demonstrate unequivocally that the band gap in lead halide perovskites indeed can be reduced significantly by inserting appropriate A-site cations in the ABX\(_3\) structure. These new materials have noncentrosymmetric structures (lacking inversion symmetry) which classifies them as potentially promising candidates in applications as ferroelectrics, communications, remote sensing in an extended spectrum region into the near and short-infrared spectrum, which is important in the night vision as long-wave infrared detectors.
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