Structure and optical properties of high light output halide scintillators

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Structural and optical properties of several high light output halide scintillators and closely related materials are presented based on first principles calculations. The optical properties are based on the Engel-Vosko generalized gradient approximation and the recently developed density functional of Tran and Blaha. The materials investigated are BaBr$_2$, BaBr, BaCl$_2$, BaF$_2$, BaI$_2$, BiI$_3$, CaI$_2$, Cs$_2$LiYCl$_6$, CsBa$_2$Br$_5$, CsBaI$_5$, K$_2$LaBr$_5$, K$_2$LaCl$_5$, K$_2$LaI$_5$, LaBr$_3$, LaCl$_3$, SrBr$_2$, and YI$_3$. For comparison results are presented for the oxide CdWO$_4$. We find that the Tran Blaha functional gives greatly improved band gaps and optical properties in this class of materials. Furthermore, we find that unlike CdWO$_4$, most of these halides are highly isotropic from an optical point of view even though in many cases the crystal structures and other properties are not. This general result is rationalized in terms of halide chemistry. Implications for the development of ceramic halide scintillators are discussed.

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I. INTRODUCTION

Scintillators are widely used in radiation detection applications including medical imaging, oil well drilling, nuclear security and high energy physics experiments. These materials function by emitting light when excited by ionizing radiation, such as gamma rays. This light is then coupled to a photomultiplier or other light detector to produce electrical signals. The performance of scintillators is characterized by their light output, normally given in terms of photons per MeV of excitation energy, proportionality (how linear the light output is as a function of excitation energy), density (related to stopping power), decay time and energy resolution. Scintillator performance depends on energy transport between the energy absorption events and the scintillation centers, suppression of non-radiative recombination channels and fast efficient light emission from the scintillation center. These scintillation centers can be intrinsic, via a mechanism such as decay of a self trapped exciton, or, as is commonly the case, at an activation center (e.g. Ce$^{3+}$ ions substituting for La$^{3+}$ in LaBr$_3$) where electron hole pairs generated by the radiation recombine. These processes are sensitive to the details of the material and in the case of materials with activators the environment of the activator ions. Halides generally have soft lattices that disfavor non-radiative recombination and can typically incorporate rare earth and other activator ions. More importantly, halide chemistry is very rich, with a wide variety of crystal structures that provide different bonding topologies for energy transfer and various environments for activator ions. In fact, one of the best known scintillators is the halide, NaI activated with Tl$^+$. This material has high light output, but is slow, non-proportional and has poor energy resolution. The finding that Ce$^{3+}$ activated LaBr$_3$ is a very high light output proportional scintillator with energy resolution better than 3% at 662 KeV has led to renewed interest in halides as scintillator hosts, especially for spectroscopic gamma ray detection. This interest has resulted in the discovery of several other interesting halide scintillators, including heavily Eu$^2$ activated SrI$_2$, which is very proportional and has a light output exceeding that of LaBr$_3$, and Ce$^{3+}$ activated YI$_3$, which is another very high light output material.

Full characterization of the optical properties of scintillators is very useful both from the point of view of improving the design of systems as regards light coupling and also importantly in selecting candidate materials for ceramic scintillators. However, full optical characterization of these halides is complicated by sensitivity to moisture and other experimental difficulties. As a result only limited data is available.

The key requirements for a ceramic scintillator are sinterability and optical isotropy. This latter requirement comes from the need to avoid light scattering at mis-oriented grain boundaries. It is commonly thought that because of this requirement cubic material is needed for a true transparent ceramic. However, radiation detection is not an optical imaging application. Therefore weak scattering and image distortion are not as detrimental as they would be in an optical application such as a ceramic lens. In fact ceramic scintillators based on monoclinic Lu$_2$SiO$_5$ (LSO) have been demonstrated. We showed in previous work that the high light output halide scintillator, SrI$_2$ is in fact very nearly optically isotropic in spite of its orthorhombic (Pbcn) crystal structure. This was an expected result considering the strongly orthorhombic lattice. It is of interest to determine whether this is the case for other high light output halide scintillators. Here we present a consistent set of first principles data for structural and optical properties of a number of high light output halide scintillators and closely related materials. We find, quite unexpectedly, that the halides we investigate have remarkably little optical anisotropy, even though a number of them are very anisotropic from...
other points of view.

II. APPROACH

The density functional calculations reported here were performed using the general potential linearized augmented planewave (LAPW) method as implemented in the WIEN2K code.11 We used well converged Brillouin zone samples and basis sets, with the standard LAPW augmentation plus local orbitals. Relativity was included at the scalar relativistic level except for BiI₃, where spin-orbit was included for the electronic structure.

The crystal structure plays a fundamental role in determining the electronic and optical properties of a material. We began our calculations by fully relaxing all free internal atomic positions consistent with the crystal symmetry for each material. The lattice parameters were held fixed at their experimental values, which are no doubt more precise than the values that can be obtained using density functional calculations. This relaxation was done using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE).13

The PBE functional, like other standard generalized gradient approximations, is based on the total energy in terms of the coupling constant averaged exchange correlation hole and is designed to reproduce the total energy. While these functionals are very useful in obtaining structures and other properties related to total energies, they underestimate, often strongly, the band gaps of most semiconductors and simple insulators. Accordingly, for the optical properties we use two other functionals. The first is the Engel-Vosko GGA (EV).14 This functional was designed to reproduce the exchange-correlation potential rather than the total energy, and gives improved band gaps.15 We used it in our prior studies on transport in PbTe and optical properties of SrI₂ and Bi₄Ge₃O₁₂ scintillators.16,17,18 The second is the semi-local functional of Tran and Blaha (TB-mBJ).19 This relatively recent functional is more sophisticated than the Engel-Vosko GGA and has been shown to give very much improved band gaps for a variety of semiconductors and insulators. We find that where comparison with experiment is possible this functional also gives very much improved band gaps as well as optical properties for these halides. As such, we focus on the results obtained using the TB-mBJ functional. The electronic structures were calculated with these two functionals based on the relaxed crystal structures from the PBE calculations. Optical properties were then obtained using the dipole matrix elements with the WIEN2K optical package.11 A 0.1 eV broadening was applied to the spectra.

III. MATERIALS AND STRUCTURES

We begin with the calculated structural parameters and brief introductions to the materials that we study.

BaF₂ is a very well characterized material. It has been applied as a scintillator, both in pure form and with activation.20–24 In pure form it has a very fast component (~0.8 ns), as well as a slow component, which can be at least partially suppressed by La doping. Fast response is of importance in applications with very high count rates or where timing is critical. It occurs in the cubic (Fm̅3m) CaF₂ structure, Ba on Wyckoff site 4a (0,0,0) and F on 8c (1/4,1/4,1/4). In our calculations we used the experimental lattice parameter,25 a=6.2001 Å.

Several of the alkaline earth di-halides, AeX₂, are high light output proportional scintillators when activated with Eu²⁺.26–29 As with BaF₂, activation with Ce³⁺ is also possible in some cases.30 Undoped BaCl₂ has a very fast response, with a short component lifetime of 1.6 ns.31 SrI₂:Eu is equal to or superior to LaBr₃:Ce³⁺ as regards light output and proportionality, although it suffers from a slower response.25 Even though the material is orthorhombic, we found it to be optically nearly isotropic.32 CaI₂:Eu²⁺ is another material with very high light output, ~ 100,000 photons/MeV.33 BaBr₂:Eu⁺ crystals have been shown to have a light output of 81,000±3,000 photons/MeV with a 662 KeV energy resolution better than 5%.34 Regarding structure, BaCl₂, BaBr₂, BaI₂ and BaIBr occur in an orthorhombic Pnma, PbCl₂ type structure with four formula units per cell. The structural parameters as determined from relaxation are given in Table I. SrBr₂ has a large tetragonal unit cell (P4/nz) with ten formula units per cell. The calculated internal parameters are as given in Table II. CaI₂ is hexagonal (P6₃/m), with Ca on site 1a (0,0,0) and I on 2d (1/2,2/3,z). In our optical calculations we used the experimental lattice parameters, a=4.49 Å, c=6.975 Å, with the calculated z=0.2535 from total energy minimization with the PBE GGA (the reported experimental value is 0.25).35

LaCl₃ and LaBr₃ activated with Ce³⁺ are very high light output, proportional scintillators with excellent energy resolution.36 They are hexagonal (P6₃/m) with the UCl₃ structure type. There are two formula units per cell, with La on site 2c (1/3,2/3,1/4) and the halogen on 6h (u,v,1/4). We used the experimental lattice parameters, a=7.4779 Å, c=4.3745 Å, for LaCl₃ (Ref. 35) and a=7.9648 Å, c=4.5119 Å, for LaBr₃ (Ref. 36). The calculated internal parameters were u=0.9145, v=0.6132 for LaCl₃ and u=0.9144, v=0.6159 for LaBr₃.

Cs₂LiYCl₆ is a member of the elpasolite family. The elpasolites are cubic Fm₃m halides, with general formula A₁₂A₂RX₆, with A₁ and A₂ alkali metals, X a halogen and R a rare earth or other trivalent element. A₁ is on site 8c (1/4,1/4,1/4), A₂ is on 4b (1/2,1/2,1/2), R is on 4a (0,0,0) and X is on 24e (u,u,u). A large number of such compounds are known.37 However, only a fraction have been studied as potential scintillator materials.38–43
TABLE I: Structural properties of orthorhombic $Pnma$ PbCl$_2$ type, BaCl$_2$, BaBr$_2$, BaI$_2$ and BaI. The lattice parameters are from experiment (Refs. 17 and 49), while the internal parameters are from total energy minimization using the PBE functional. For BaBr, X1 is I and X2 is Br. All atoms are on Wyckoff site 4c with y=0.25.

|       | BaCl$_2$ | BaBr$_2$ | BaI$_2$ | BaI   |
|-------|----------|----------|---------|-------|
| a (Å) | 7.87     | 8.27     | 8.922   | 8.65  |
| b (Å) | 4.73     | 4.95     | 5.304   | 5.12  |
| c (Å) | 9.41     | 9.19     | 10.695  | 10.31 |
| Ba     | x        | 0.2481   | 0.2470  | 0.2466|
|        | z        | 0.3838   | 0.1166  | 0.1228|
| X1     | x        | 0.1423   | 0.6426  | 0.6424|
|        | z        | 0.0708   | 0.0714  | 0.0721|
| X2     | x        | 0.5274   | 0.5266  | 0.5246|
|        | z        | 0.8313   | 0.6686  | 0.6665|

TABLE II: Internal structural coordinates of tetragonal $P4/n$ (No. 85) SrBr$_2$ as determined by total energy minimization. The lattice parameters were fixed at their experimental values of a=11.630 Å, and c=7.146 Å. (Ref. 53)

|       | Sr1 | Sr2 | Br1 | Br2 | Br3 | Br4 |
|-------|-----|-----|-----|-----|-----|-----|
| x     | 0.4141 | 0.7500 | 0.5402 | 0.5426 | 0.2500 | 0.2500 |
| y     | 0.6035 | 0.7500 | 0.6527 | 0.8386 | 0.7500 | 0.7500 |
| z     | 0.7520 | 0.1487 | 0.3761 | 0.9004 | 0.0000 | 0.5000 |

Cs$_2$LiYCl$_6$ is of particular interest because of its high Li content, which makes it useful as a neutron detector. We used the experimental lattice parameter for Cs$_2$LiYCl$_6$ from Reber and co-workers, with $a=10.4857$ Å, with the calculated internal parameter $u=0.2517$ (an experimental value of 0.25046 was reported by Reber and co-workers).

The scintillation properties of Ce$^{3+}$ activated K$_2$LaCl$_5$, K$_2$LaBr$_5$ and K$_2$LaI$_5$ were investigated by van Loef and co-workers. These isotructural orthorhombic compounds showed high light output, up to 55,000 photons / MeV (for K$_2$LaI$_5$:Ce$^{3+}$). The iodide also showed a reasonable decay time of 24±5 ns and 662 KeV energy resolution of 4.5±0.5%, although use of this scintillator is complicated because of self-activity associated with K. Our calculated structural properties are given in Table III.

CsBa$_2$Br$_5$ and CsBa$_2$I$_5$ occur in a monoclinic $P2_1/c$ (No. 14) structure. Eu$^{2+}$ doped CsBa$_2$I$_5$ was reported to have a light yield of approximately 97,000 photons per MeV and to be less hygroscopic than LaBr$_3$ or SrI$_2$. The calculated structural parameters are as given in Table IV.

Y$_3$I$_2$ and BiI$_3$ are related materials. Ce$^{3+}$ activated Y$_3$I$_2$ was recently reported to have a very high light yield of almost 100,000 photons per MeV. The related compound BiI$_3$ is of interest mainly as a semiconductor for radiation detection, rather than as a scintillator. We include it here for comparison with Y$_3$I$_2$. Unlike Y$_3$I$_2$, BiI$_3$ has substantial covalency between Bi 6p and halogen p states, which leads to enhanced Born charges and may be expected to affect the optical properties. These compounds occur in a rhombohedral $R3$ structure, with the cations on site 6c (0,0,z) and I on 18f (u,v,w).

IV. ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES

As mentioned, three functionals were used in the present study, the PBE GGA for the structural properties, and the Engel-Vosko and TB-mBJ functionals for the optical properties. The recently developed TB-
FIG. 1: Calculated band structure of BaF$_2$ with the three functionals. mBJ has been shown to give much more accurate band gaps than other semilocal functionals in a wide variety of materials. As such, we emphasize results obtained using that functional. For comparison, the fundamental band gaps of the compounds studied are listed in Table V. The EV gaps are invariably intermediate between those of the standard PBE and the TB-mBJ functionals with the exception of the La containing compounds. In those compounds, the $f$-resonance is found inside the insulating gap for all three functionals. The position of the $f$-resonance relative to the valence band edge depends on the compound, but for a given material is practically unchanged between the different functionals. For these compounds we show both the gap between the valence band maximum and the bottom of the $f$-bands making up the resonance, as well as the gap between the valence bands and the non-$f$ conduction bands. Experimental band gaps are unavailable for most of these materials. We start with BaF$_2$, which as mentioned is a relatively well characterized material. The calculated band structure with the PBE, EV and TB-mBJ functionals is as shown in Fig. 1, while the corresponding electronic density of states (DOS) is given in Fig. 2. The PBE band structure has a direct gap at Γ that is clearly underestimated with respect to experiment. The valence bands, of F $p$ character, are narrow with a width of less that 2 eV, while the metal derived conduction bands are more dispersive. The EV band structure is similar to the PBE result but with a somewhat larger band gap. The mBJ band structure has a considerably enhanced gap of 9.8 eV. Furthermore, the conduction bands are distorted relative to the PBE result, with the conduction band minimum now at the X point, although it should be noted that the distinction between direct and indirect is not so important for the properties of this compound because of the very flat valence bands.

The experimental band gap of BaF$_2$ is usually quoted as 11 eV based on the measured ultraviolet reflectance spectrum. This spectrum shows several features near the gap: a prominent feature at 10.00 eV, assigned as an exciton, a weaker feature at 10.57, also assigned as an exciton, and a direct band edge at 11.0 eV. Subsequent two photon absorption experiments assigned the gap as 10.6 eV. The TB-mBJ direct gap at $X$ of 9.90 eV is $\sim$ 1 eV lower. Importantly, the experimental spectrum has three large peaks in the valence band region below 16 eV. The calculated TB-mBJ reflectance spectrum is shown in Fig. 3. There are two prominent peaks that can

TABLE V: Calculated fundamental band gaps in eV for the various compounds. For La containing compounds we list both the band gap from the valence band edge to the La 4$f$-resonance (denoted $f$) and to the conduction bands excluding the resonance (denoted cb, see text). Spin orbit is included for BiI$_3$.

|        | PBE   | EV    | TB-mBJ |
|--------|-------|-------|---------|
| BaF$_2$| 6.87  | 7.46  | 9.77    |
| BaCl$_2$| 5.23  | 5.66  | 6.45    |
| BaBr$_2$| 4.45  | 4.85  | 5.39    |
| BaIBr$_3$| 3.79  | 4.13  | 4.45    |
| BaI$_2$ | 3.50  | 3.87  | 4.14    |
| CaI$_2$ | 3.49  | 3.92  | 4.26    |
| SrBr$_2$| 4.99  | 5.25  | 5.91    |
| YI$_3$ | 2.81  | 3.02  | 3.31    |
| BiI$_3$| 1.43  | 1.67  | 1.82    |
| Cs$_2$LiYCl$_6$| 4.90 | 5.30  | 5.97    |
| CsBa$_2$Br$_5$| 4.53 | 5.13  | 5.77    |
| CsBa$_2$I$_5$| 3.69 | 4.14  | 4.49    |
| K$_2$LaCl$_5$$f$| 4.46 | 4.46  | 4.59    |
| K$_2$LaCl$_5$ cb| 5.23 | 5.49  | 6.32    |
| K$_2$LaBr$_5$$f$| 3.69 | 3.76  | 3.74    |
| K$_2$LaBr$_5$ cb| 4.33 | 4.66  | 5.26    |
| K$_2$LaI$_5$$f$| 2.79 | 2.95  | 2.80    |
| K$_2$LaI$_5$ cb| 3.38$^*$| 3.61  | 3.99    |
| LaCl$_4$$f$| 3.97 | 4.04  | 4.15    |
| LaCl$_4$ cb| 4.95 | 5.26  | 5.82    |
| LaBr$_3$$f$| 3.20 | 3.28  | 3.24    |
| LaBr$_3$ cb| 3.98 | 4.24  | 4.60    |

$^*$f-resonance overlaps bottom of conduction band.

FIG. 2: (color online) Electronic density of states of BaF$_2$ as calculated with the PBE, EV and TB-mBJ functionals.
be matched with the upper two peaks in the experimental spectrum (Ref. 59) using a band shift of \( \sim 1 \) eV. This is consistent with the assignment of the lower experimental peak as excitonic and the conclusion that the TB-mBJ band gap is underestimated by \( \sim 1 \) eV.

The calculated refractive index is shown as a function of energy for the three functionals in Fig. 4. The refractive indices follow the trend in the band gaps, with the result of the TB-mBJ functional lowest. Experimentally, the refractive index of BaF\(_2\) is practically constant, rising from \( n=1.465 \) at low energy to \( n_D=1.474 \) at 589 nm (2.107 eV).\(^{58}\) This is in close agreement with the results using the TB-mBJ functional. We obtain a low frequency value of \( n=1.56 \) with a weak dispersion as in experiment. The low frequency PBE value is higher at \( n=1.56 \) and shows a stronger energy dependence consistent with the smaller gap, while the EV value of \( n=1.52 \) is intermediate.

This result shows that the TB-mBJ functional not only improves the band gap, but also improves the optical response of this halide relative to the PBE functional, which is regarded as state of the art for calculations of total energies. This is important because the response depends not only on band energies but also on the wavefunctions, specifically through the dipole matrix elements. The charge density and total energy are fundamental quantities within density functional theory while the single particle energies are not. It is strongly thought that the Kohn-Sham eigenvalues of the exact density functional will not produce correct band gaps in insulators, even though its charge density and static response will be exact.\(^{60}\) Therefore it is of interest to note that the improvement in the band gap of semi-local functionals, particularly going to the EV and then the TB-mBJ functional improve the static response at the same time as they improve the band gap. In the following we focus on results obtained with the TB-mBJ functional.

The calculated TB-mBJ band gap of 5.97 eV for the high light output elpasolite scintillator, Cs\(_2\)LiYCl\(_6\) agrees well with the experimental onset of optical absorption at 5.9 eV. The refractive index is shown in Fig. 5.\(^{38}\) The low frequency limit is \( n=1.65 \). There is more dispersion than in BaF\(_2\), but the spectrum is otherwise featureless almost up to the band edge. We are not aware of experimental measurements of the optical properties of this material.

The isostructural tri-iodides, YI\(_3\) and BiI\(_3\) offer an interesting contrast. As mentioned, when activated with Ce\(^{3+}\), YI\(_3\) is a very high light output scintillator, while BiI\(_3\) is not. The emission of YI\(_3\):Ce\(^{3+}\) starts at \( \sim 2.9 \) eV and peaks at 2.26 eV.\(^{7}\) The high energy onset is below our calculated TB-mBJ gap of 3.31 eV, but is higher than the gap obtained with the standard PBE GGA and prior calculations done with the local density approximation (LDA).\(^{61}\) The difference between YI\(_3\) and BiI\(_3\) can be understood in terms of the electronic structure, specifically that the band gap of BiI\(_3\) is too small and that this is due to low lying Bi 6p states.

In order for scintillation to take place an electron hole pair must recombine at the Ce\(^{3+}\) site. For this to be efficient both the upper and lower states for the activator ion should be in the band gap. This is evidently not possible in BiI\(_3\). As mentioned, the Ce\(^{3+}\) emission in YI\(_3\) has a high energy onset of 2.9 eV, which is similar to that in other iodides. This is a lower bound on the en-

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FIG. 3: Calculated TB-mBJ reflectivity spectrum of BaF\(_2\).

FIG. 4: (color online) Calculated refractive index of BaF\(_2\) with the three functionals.

FIG. 5: (color online) Calculated refractive index of Cs\(_2\)LiYCl\(_6\).
FIG. 6: (color online) Comparison of the electronic DOS of YI₃ and Bi₃ as obtained with the TB-mBJ functional.

FIG. 7: (color online) Calculated refraction of YI₃ (top) and Bi₃ (bottom) as a function of energy based on the TB-mBJ functional.

Energy difference between the upper and lower states of the activator ion. A comparison of the calculated TB-mBJ electronic DOS of the two materials is given in Fig. 6. The lowest conduction bands in YI₃ are formed from Y 4d states. In contrast, there is a manifold of Bi 6p states making up the conduction bands in BiI₃, and these occur at lower energy. This leads to a 1.49 eV lower band gap in the Bi compound. Our TB-mBJ gap for BiI₃ is substantially higher than that obtained in prior calculations using other functionals, but it is still only 1.82 eV. The experimental optical gap is 2.0 eV. This does not leave a sufficient energy range for both the upper and lower states to be in the gap. This is similar to the problem in activating Pb phosphate glasses with rare earths. In fact, considering the fact that, all things being equal, lower gaps favor higher light output, but that too low a gap prevents activation, the gap of YI₃ is probably close to optimum for a Ce³⁺ activated material.

The refractive indices of YI₃ and BiI₃ are presented in Fig. 7. Surprisingly, the refractive index of YI₃ is almost isotropic, even though the material itself is structurally very anisotropic as shown in Fig. 8. The low energy limits of the refractive indices of YI₃ are nₓₓ = 2.08 and nₜₜ = 2.06, which is an anisotropy of 1%. BiI₃ is slightly less isotropic, but is still remarkably so for such an anisotropic layered crystal structure. The low energy refractive indices are nₓₓ = 2.76 and nₜₜ = 2.71 for BiI₃. Jellison and co-workers reported a value of 3.1 at 1.6 eV. For comparison, our calculated values at 1.6 eV are 3.16 in-plane (ₓₓ) and 3.02 out-of-plane (ₜₜ), in excellent agreement with the experiment.

We find a similar remarkable near isotropy of the optical properties in several other halides as well. This is the case even for monoclinic CsBa₂Br₅ and CsBa₂I₅ as shown in Fig. 8. The three diagonal components of the refractive index are practically the same almost up to the band edge, while the off-diagonal component associated with the monoclinic symmetry is practically zero over this energy range.

For comparison, we also performed calculations for monoclinic CdWO₄. We followed the same procedure relaxing the internal coordinates using the PBE functional and then performing optical calculations using the TB-mBJ functional. The calculated band gaps are 2.99 eV with the PBE functional and 4.16 eV with the TB-mBJ
form. The PBE value is similar to that obtained previously by Abraham and co-workers.\textsuperscript{68} The TB-mBJ value is close to the experimental value of 3.8 – 4.1 eV (see Ref. \textsuperscript{68}). The refractive index is shown in Fig. 10. As may be seen, in contrast to the halides, it is quite anisotropic with a substantial off-diagonal component.

Returning to halides, we next discuss La containing materials. The band structure of these materials may be described as that of an equivalent material based on a simple trivalent ion, e.g. Y, plus additional unoccupied $f$ derived bands that occur in the band gap. The $f$ bands comprise the so-called $f$-resonance. In Table \textsuperscript{V} we give both the value of the fundamental gap, which is from the top of the halogen $p$ derived valence bands to the bottom of the $f$-resonance as well as a larger gap, denoted “cb”, which is from the top of the valence bands to the bottom of the conduction bands, excluding the $f$-resonance.

We find that in contrast to the band gaps of the other materials studied, the fundamental gap of these materials is practically unchanged upon going from the PBE to the TB-mBJ functional. That is the position of the $f$ bands relative to the valence band maximum is almost the same with these three functionals. This is illustrated for LaBr\textsubscript{3} and K\textsubscript{2}LaBr\textsubscript{5} in Fig. 11. The position of the higher lying non-$f$ conduction bands is, however, increased with the TB-mBJ functional. This does lower the optical refractive index, even though the fundamental band gap is unchanged.

The calculated refractive indices of LaCl\textsubscript{3} and LaBr\textsubscript{3} are shown in Fig. 12. The low energy values are $n_{xx}=1.87$ and $n_{zz}=1.91$ for LaCl\textsubscript{3} and $n_{xx}=2.04$ and $n_{zz}=2.09$ for LaBr\textsubscript{3}. This follows the expected trend where bromides have higher refractive index than chlorides. Again, we find low anisotropy in materials that are structurally

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**FIG. 9**: (color online) Calculated refraction for CsBa\textsubscript{2}Br\textsubscript{5} (top) and CsBa\textsubscript{2}I\textsubscript{5} (bottom) based on the TB-mBJ functional.

**FIG. 10**: (color online) Calculated refraction for CdWO\textsubscript{4} with the TB-mBJ functional.

**FIG. 11**: (color online) Comparison of the DOS with the three functionals for LaBr\textsubscript{3} (top) and K\textsubscript{2}LaBr\textsubscript{5} (bottom). Note that the position of the $f$-resonance that sets the fundamental gap is relatively unaffected by the changes in functional.
anisotropic. The same trend with halogen atomic number and also very low optical anisotropy is found in K$_2$LaCl$_5$, K$_2$LaBr$_5$ and K$_2$LaI$_5$, as shown in Fig. 13. The calculated TB-mBJ band gap to the non-$f$ upper conduction band edges (“cb”) for K$_2$LaCl$_5$, K$_2$LaBr$_5$ and K$_2$LaI$_5$ are 6.32 eV, 5.26 eV and 3.99 eV, respectively, as compared to the experimental estimates of 6.6 eV, 5.5 eV and 4.5 eV$^{45,46}$.

The refractive indices of BaCl$_2$, BaBr$_2$, BaIBr and BaI$_2$ are given in Figs. 14, while those of CaI$_2$ and SrBr$_2$ are given in Figs. 15 and 16 respectively. The calculated TB-mBJ band gap for BaCl$_2$ of 6.45 eV is in reasonable accord with the estimate from Cl-K x-ray spectroscopy of 7.0 eV.$^{49}$ As mentioned, BaCl$_2$, BaBr$_2$, BaIBr and BaI$_2$ occur in a complex orthorhombic $Pnma$ structure. SrBr$_2$ is tetragonal, while CaI$_2$ is rhombohedral. None of these materials is cubic. CaI$_2$ activated with Eu$^{2+}$ has been known to be an extremely high light output material since the 1960’s.$^{26}$ However, this hexagonal material has not been used in applications because of crystal growth problems due to its platelet growth habit. Nonetheless, again we find only very small anisotropy in the optical properties for all of these materials, similar to what we found previously for SrI$_2$.$^{39}$

FIG. 12: (color online) Calculated refraction for LaCl$_3$(top) and LaBr$_3$ (bottom) based on the TB-mBJ functional.

V. DISCUSSION

We have two main conclusions, besides the numerical data, which we hope will be useful in improving the design of scintillator systems for better light coupling. First of all, we find that the newly developed TB-mBJ functional greatly improves both the band gaps and the optical properties in a broad class of halide materials, consistent with results reported for other compounds.$^{19}$ Considering the computational efficiency of this method, which is similar to standard density functional methods, we expect that this method will enable optical character-
Qualitatively, it may be understood from the coordination environments and general band structure features. In particular, these materials have relatively wide band gaps due to the large electronegativity difference between the cations and the halogen atoms. The halogen $p$ derived valence bands are narrow compared to typical metal oxides. This narrow band width suggests that one can understand the properties in real space instead of depending essentially on detailed band dispersions. Additionally, the valence band formation comes at least largely from direct hopping between the halogen $p$ orbitals on adjacent sites these materials. The structures can be described in
anion contact terms. From a structural point of view, the anion lattices of these compounds are distortions of high symmetry structures, with most of the anisotropy coming from the cation placement in the intertices of the anion lattice. This places the cations in locally highly symmetric cages based on high nearest neighbor anion coordination numbers. Since the anion bands are relatively non-dispersive, the main crystal structure dependence comes from the conduction bands. Therefore, the small optical anisotropy of these materials can be rationalized in terms of the highly symmetric local environments of the cations as far as nearest neighbor anion coordination is concerned. Further work to elucidate this is clearly needed.

In any case, this result has important implications for the development of halide scintillators. Gamma spectroscopy requires high quality uniform crystals of sufficient size to effectively stop the Gamma rays in the scintillator volume. This typically requires cm sized crystals, and many applications benefit from still larger sizes. As a result, crystal growth is one of the main challenges in the development of new halide scintillators. The near optical isotropy of these materials, however, suggests that ceramic scintillators of sufficient size to be useful for Gamma spectroscopy can be made. While this will require solution of a number of problems, for example, the development of methods to produce dense sintered bodies without contamination in these often hygroscopic, air sensitive materials, it may enable the use of low symmetry difficult to grow halide materials for gamma spectroscopy and other scintillator applications. Furthermore, ceramic materials are generally lower cost than single crystals, especially if large volumes of material are needed.

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