

A systematic search for new scintillators using electronic structure calculations

M. Klintonberg^{*,**}, S. E. Derenzo^{*} and M. J. Weber^{*}

^{*}Lawrence Berkeley National Laboratory, University of California, Berkeley, USA¹

^{**}Department of Physics, Uppsala University, Uppsala, Sweden

ABSTRACT

A systematic study of several hundred inorganic crystal structures have been performed by means of electronic structure calculations with the goal of finding potential new scintillator materials for synthesis and testing. All X-ray or neutron diffraction measurements of crystals containing one or more of the heavy elements Tl, Hg, Pb or Bi and with all sites in the unit cell fully occupied were extracted from the Inorganic Crystal Structure Database (ICSD). A Full-Potential Linear Muffin-Tin Orbital (FP-LMTO) implementation with a LDA exchange-correlation energy functional was used for solving the electronic structure. The data was analyzed for density, photoelectric fraction at 511 keV, direct/indirect band gap, LDA band gap energy, energy dispersion, bandwidths, degree of covalency, electronic density distribution of upper valence electrons, electron and hole masses, valence and conduction band parity, etc. Preliminary computational results are presented for a number of representative materials.

Keywords: Wide band-gap semiconductors; electronic structure calculations; inorganic crystals; scintillation; semiconductors;

1 INTRODUCTION

There is a need for new bright, ultrafast scintillators for medical imaging, high energy and nuclear physics, and other applications. Although many different scintillation phenomena and materials have been explored and exploited, [1] relatively little attention has been given to the use of near-edge emission from wide band gap semiconductors where fast electron-hole recombination is possible. More than three decades ago Lehman [2-4] demonstrated that by n-doping ZnO and CdS with Ga and In, respectively, and preparing the materials under reducing conditions, quenching could be reduced and edge emission with high luminosity and ultrafast decay times (< 1 ns) could be realized.

Here we present a first-principles computational approach for identifying potential new scintillator materials for edge emission. The initial survey focuses on finding appropriate dense, covalent host materials; the next step would model suitable dopants for generating donor and acceptor levels. The Inorganic Crystal Structure Database

(ICSD) [5] was utilized to obtain structural data for electronic band structure calculations. It contains more than 3000 entries of crystals that contain one or more of the heavy elements Hg, Tl, Pb, or Bi. Thus far we have investigated the sub-group of these materials where all sites in the unit cell are fully occupied. This subgroup numbers ~1200 compounds. Techniques for handling fractionally occupied sites (this will include a super-cell approach) are currently under development.

2 COMPUTATIONAL APPROACH

2.1 The electronic structure

The theoretical framework used for this project is Density Functional Theory (DFT). More specifically we use a Full-Potential Linear Muffin-Tin Orbital (FP-LMTO) technique [6-8] and the Local Density Approximation (LDA) exchange-correlation energy functional [9]. Relativistic effects, that are important for the heavier compounds, are taken into account. FP implies that no inherent geometrical approximations have been used in the theory meaning that this approach can be used when investigating different crystallographic systems, c.f. LMTO-ASA (atomic sphere approximation)[6], which is computationally more efficient but constrained to specific geometries.

DFT is based on two statements i) the ground state expectation value of any observable, including the total energy, is a unique functional of the exact ground state density $n(r)$, and ii) the exact ground state density minimizes the total energy functional $E(n(r))$. These statements lead to the Schrodinger like Kohn-Sham equations

$$H_{eff}\psi_i(r) = [-\nabla^2 + V_{eff}(r)]\psi_i(r) = \epsilon_i\psi_i(r),$$

where $\{\epsilon_i, \psi_i \mid \epsilon_1 < \epsilon_2 < \epsilon_3 \dots\}$

are the Kohn-Sham eigenvalues and eigenfunctions (orbitals), i.e. the solutions to our problem. The realization of Kohn and Sham was that the full minimization problem could be formulated in terms of a set of single particle problems in an effective potential, $V_{eff}(r)$ [10].

In the FP-LMTO method the unit cell is divided into two different regions: 1) the muffin-tins surrounding each atom site and 2) the interstitial region which forms the rest of the

¹ mkkintonberg@lbl.gov, sederenzo@lbl.gov, mjweber@lbl.gov

unit cell. The muffin-tin radii are maximized but constrained not to overlap. Inside the muffin-tin spheres the density and potential are expanded using a radial function times a sum of spherical harmonics that is invariant under the space group. In the interstitial region where the different functions fluctuate less, a sum of plane waves is used in the expansion (Fourier sums). The basis functions of the interstitial region are Bloch sums of Neumann and Hankel functions; inside the muffin-tin spheres the Neumann or Hankel functions are augmented by a numerical basis function.

2.2 The Inorganic Crystal Structure Database

The ICSD has been used for obtaining the structural information needed for the construction of the periodic real space unit cell. The irreducible cell, space group (with associated transformations), and unit cell dimensions are the inputs to a code that transforms the irreducible cell into real space and at the same time computes crystallographic properties such as density, coordination geometry, and photoelectric fraction at 511 keV (of interest for positron emission tomography (PET) detectors).

3 SELECTION CONSIDERATIONS

For surveying the many hundred different compounds we focus on the following properties: density, photoelectric fraction, direct/indirect energy dispersion structure, LDA band gap, covalency, effective mass of electrons and holes, bandwidths of the valence and conduction bands, and potential core valence luminescence materials. In this study we restricted the initial survey to materials containing one or more of the heavy elements Hg, Tl, Pb or Bi and with all sites in the unit cell fully occupied. The main reason for imposing the latter restrictions is the immense amount of computational time needed for hundreds of FP-LMTO calculations.

3.1 Crystallographic structure associated properties

Given the irreducible cell, space group and unit cell parameters, it is straightforward to calculate the density of the crystal, local coordination geometries and nearest neighbor distances. The photoelectric fraction is computed using known atomic photoelectric and Compton cross-sections that are found in the literature.

3.2 Electronic structure associated properties

Because the systems under investigation are periodic, Bloch's theorem imposes a k -dependence of the energy eigenvalues and eigenfunctions. This is most easily viewed in energy dispersion diagrams, the band structure

plot where the energies are plotted versus k for each eigenstate.

Direct transitions involve no change in k , i.e. the top of the valence band is at the same k vector as the bottom of the conduction band; the transition is indirect otherwise. The difference in energy between these two bands is the LDA band gap. The LDA band gap is well known to underestimate the real gap but can be resolved using the computationally more demanding GW correction [11-13]. To obtain information about the covalency, the curvature of the top of the valence band and the bottom of the conduction band is investigated. The interstitial charge density is another measure of covalency.

4 RESULTS AND CONCLUDING REMARKS

Preliminary results for a number of oxide, halide, and chalcogenide materials are summarized in Table 1. The first five entries are semiconducting compounds with well known ultra-fast scintillation. We have measured the ultra-fast scintillation of these compounds (ZnO, CdS, CuI, PbI₂ and HgI₂).[14] We have also synthesized BiOI, BiOF, PbBrF, Bi₂O₃ and Ag₂HgI₄ and searched for ultra-fast scintillation. None of these latter materials exhibited ultra-fast scintillation indicating further selection criteria and more detailed analyses are needed.

In Table 1 several of the compounds have been structurally determined by many different groups, thus resulting in slightly different structures. Only when the calculated electronic structures deviated by more than a few percent the additional entries for the compound have been included in Table 1.

Because we are interested in covalent materials with ultra-fast near-band-edge emission, it is crucial that the charge carriers do not become deeply trapped. Similarly, for doped materials there should not be large geometric relaxation around the impurities thus creating potentially deep electron or hole traps. Future calculations will include the geometric relaxation of supercells, with and without excited states. In addition, calculations of the effective masses of electrons and holes will be used to predict free exciton binding energies and radii.

To our knowledge this is the first study of potential scintillator materials wherein a large number of compounds have been investigated using the same computational approach throughout the entire study. This allows us to compare properties of the different compounds directly.

Table 1 Summary of data for direct gap materials obtained from FP-LMTO electronic structure calculations. The columns show compound, Schonflies symbol (Sfs), density (ρ) in g/cm³, photoelectric fraction at 511keV (pef) and the LDA band gap in eV, respectively.

Compound	Sfs	ρ	pef	LDA
ZnO	Γ_h	5.73	0.03	0.79

Compound	Sfs	ρ	pef	LDA
CdS	Γ_h	4.82	0.13	0.95
CuI	Γ_c^f	5.73	0.16	0.62
PbI ₂	Γ_h	6.10	0.40	1.65
HgI ₂	Γ_q	6.43	0.38	0.78

BiF ₃	Γ_c	8.76	0.47	2.97
CsPbF ₃	Γ_c	5.96	0.40	1.78
RbPbF ₃	Γ_c	5.28	0.40	1.91
TlBr	Γ_c	7.47	0.45	2.00
TlPF ₆	Γ_c	4.64	0.38	6.17
Cs ₂ NaBiCl ₆	$\Gamma_{c,ff}$	3.71	0.30	2.93
Cs ₂ PbCl ₆	$\Gamma_{c,ff}$	4.03	0.30	1.36
Cs ₂ TlBiF ₆	$\Gamma_{c,ff}$	5.72	0.41	1.84
Hg ₂ Zn ₂ F ₆ O	$\Gamma_{c,ff}$	7.97	0.37	0.39
HgF ₂	$\Gamma_{c,ff}$	9.32	0.46	0.37
K ₂ NaTlF ₆	$\Gamma_{c,ff}$	4.28	0.33	4.24
Pb ₂ Sb ₂ O ₇	$\Gamma_{c,ff}$	9.09	0.40	0.03
PbS	$\Gamma_{c,ff}$	7.60	0.49	0.03
PbTe	$\Gamma_{c,ff}$	8.33	0.44	0.30
Rb ₂ PbCl ₆	$\Gamma_{c,ff}$	3.70	0.28	1.20
Tl ₂ NaRhF ₆	$\Gamma_{c,ff}$	6.95	0.41	1.44
Tl ₂ SnCl ₆	$\Gamma_{c,ff}$	4.96	0.38	2.60
TlBr	$\Gamma_{c,ff}$	6.59	0.45	2.17
TlCl	$\Gamma_{c,ff}$	6.31	0.48	2.01
TlClO ₄	$\Gamma_{c,ff}$	4.58	0.41	0.65
TlI	$\Gamma_{c,ff}$	6.58	0.44	2.07
Tl ₃ VS ₄	$\Gamma_{c,v}$	5.68	0.45	1.30
Tl ₃ VS ₄	$\Gamma_{c,v}$	6.23	0.45	1.74
Bi _{0.67} NbS ₂	Γ_h	5.95	0.36	0.22
Bi ₂ Ge ₃ O ₉	Γ_h	6.23	0.38	2.95
BiI ₃	Γ_h	5.83	0.37	1.21
Pb ₂ Bi ₂ Se ₅	Γ_h	7.58	0.44	0.07
Pb ₅ (PO ₄) ₃ Cl	Γ_h	7.19	0.45	2.44
PbI ₂	Γ_h	6.09	0.40	1.63
TlSbO ₃	Γ_h	7.14	0.40	0.17
TlSbO ₃	Γ_h	7.14	0.40	2.04
(Hg ₂ (OHg) ₂)(NO ₃) ₂	Γ_m	7.55	0.46	1.70
Ag ₂ HgS ₂	Γ_m	7.84	0.33	0.32
Bi ₂ Cu(SeO ₃) ₄	Γ_m	5.66	0.33	2.08
Cs ₂ HgI ₄	Γ_m	4.82	0.30	1.83
CsHg ₂ Br ₅	Γ_m	5.51	0.33	1.94
CsTlI ₄	Γ_m	5.02	0.32	1.14
Hg ₃ O ₂ Cl ₂	Γ_m	8.65	0.46	0.19
HgSeO ₄ (H ₂ O)	Γ_m	5.62	0.35	1.32
K ₄ Na ₂ (Tl ₂ O ₆)	Γ_m	4.48	0.37	1.16
Pb ₂ (As ₂ O ₅)	Γ_m	6.89	0.41	2.85
Pb ₄ (SiO ₄)Br ₄	Γ_m	6.72	0.43	2.79
Pb(HAsO ₄)	Γ_m	6.04	0.39	2.82
Pb(SO ₃)	Γ_m	6.46	0.44	2.97
Pb(SeO ₃)	Γ_m	7.05	0.41	2.59
Pb(SeO ₃)	Γ_m	7.08	0.41	0.86
PbAs ₂ O ₄	Γ_m	5.96	0.35	2.69
PbCu(P ₂ O ₇)	Γ_m	5.33	0.32	0.24
Tl(NbO)(P ₂ O ₇)	Γ_m	4.46	0.31	0.44
TlSbF ₄	Γ_m	6.17	0.38	3.73
TlSnF ₇	Γ_m	6.08	0.34	1.89

BaPbO ₃	Γ_m^b	8.38	0.41	0.13
Bi(SbO ₄)	Γ_m^b	8.46	0.40	2.53
BiBr	Γ_m^b	7.08	0.46	0.33
BiI	Γ_m^b	7.01	0.46	0.05
BiI	Γ_m^b	7.10	0.46	0.12
BiVO ₄	Γ_m^b	6.94	0.42	1.95
Cd(HgO ₂)	Γ_m^b	9.52	0.39	0.62
Cs ₂ (Hg ₃ I ₈)	Γ_m^b	5.31	0.34	1.46
Cs ₄ PbCl ₆	Γ_m^b	3.79	0.28	3.66
Cs(Hg ₅ Cl ₁₁)	Γ_m^b	5.17	0.40	2.60
Cu ₄ Bi ₅ S ₁₀	Γ_m^b	6.39	0.42	0.41
K(BiO ₂)	Γ_m^b	6.13	0.46	1.72
Li ₂ PbO ₃	Γ_m^b	6.94	0.46	1.17
NaBiO ₂	Γ_m^b	7.01	0.47	1.44
Pb ₅ S ₂ I ₆	Γ_m^b	6.74	0.42	1.28
Rb(BiO ₂)	Γ_m^b	6.44	0.43	1.91
Tl _{0.5} V ₂ O ₅	Γ_m^b	4.66	0.27	4.14
Tl ₂ SnS ₃	Γ_m^b	6.37	0.43	0.76
TlCu ₃ S ₂	Γ_m^b	7.00	0.32	0.31
AgHg ₂ PO ₄	Γ_o	8.18	0.41	1.35
Ba ₂ HgS ₃	Γ_o	5.65	0.33	1.27
BaHgSnS ₄	Γ_o	5.02	0.31	1.62
Cs ₂ (HgBr ₄)	Γ_o	4.64	0.28	2.42
Cs ₃ HgCl ₅	Γ_o	3.98	0.29	2.93
HgCl ₂	Γ_o	5.62	0.41	2.49
K ₂ HgCl ₄	Γ_o	3.26	0.31	0.26
KHGf ₃	Γ_o	5.75	0.40	0.16
KTlBr ₄	Γ_o	4.36	0.29	1.72
Pb ₂ Mg(WO ₆)	Γ_o	9.26	0.45	1.99
Pb(SO ₃)	Γ_o	6.44	0.44	3.38
Pb(TiO ₃)	Γ_o	7.71	0.42	2.16
Pb(ZrO ₃)	Γ_o	8.03	0.40	2.47
PbCrO ₄	Γ_o	6.21	0.41	2.20
PbSO ₃	Γ_o	6.47	0.44	3.29
Tl ₄ (Cu ₂ I ₆)	Γ_o	6.91	0.39	1.19
Ba ₂ BiRuO ₆	Γ_o^b	7.13	0.33	0.32
Bi ₂ TeO ₆	Γ_o^b	9.08	0.44	1.93
Cs ₂ PbO ₃	Γ_o^b	6.46	0.37	1.34
K ₂ PbO ₃	Γ_o^b	4.91	0.40	0.69
Li ₄ PbO ₄	Γ_o^b	5.02	0.43	1.74
PbSO ₄ (PbO) ₂	Γ_o^b	7.06	0.48	0.93
PbTlI ₃	Γ_o^b	6.45	0.41	1.66
Rb ₂ PbO ₃	Γ_o^b	5.80	0.36	0.53
Compound	Sfs	ρ	pef	LDA
Tl ₄ CrI ₆	Γ_o^b	6.92	0.40	0.12
TlF	Γ_o^f	8.57	0.50	1.77
BiPS ₄	Γ_o^v	4.22	0.38	0.96
TlCu(CuO ₂)	Γ_o^v	8.06	0.37	0.23
Ag ₂ HgI ₄	Γ_q	6.02	0.29	0.75
AgPbOBr	Γ_q	7.78	0.38	0.18
Bi ₂ CuO ₄	Γ_q	8.62	0.47	0.98
Bi ₂ O ₃	Γ_q	9.17	0.51	0.34
BiOF	Γ_q	9.22	0.50	2.73
BiOI	Γ_q	9.69	0.44	1.18
Cu ₂ HgI ₄	Γ_q	6.12	0.29	0.26
Hg ₂ PbI ₂ S ₂	Γ_q	7.35	0.43	1.36
HgI ₂	Γ_q	6.35	0.38	0.76

Pb ₂ Br ₂ CO ₃	Γ_q	6.69	0.42	2.50
Pb ₂ Cl ₂ (CO ₃)	Γ_q	6.12	0.45	2.79
Pb ₃ O ₄	Γ_q	8.71	0.50	1.24
Pb ₃ O ₄	Γ_q	8.96	0.50	0.65
Pb(TiO ₃)	Γ_q	7.98	0.42	2.34
Pb(TiO ₃)	Γ_q	8.04	0.42	2.59
PbBrF	Γ_q	7.67	0.43	2.73
PbClF	Γ_q	7.13	0.47	3.11
PbClF	Γ_q	7.21	0.47	3.10
Tl ₄ CdI ₆	Γ_q	6.88	0.40	1.78
Tl ₄ CrI ₆	Γ_q	6.71	0.40	0.15
Tl ₄ HgBr ₆	Γ_q	7.00	0.43	1.81
Tl ₄ HgI ₆	Γ_q	7.15	0.43	1.27
Tl ₅ Se ₂ Cl	Γ_q	8.64	0.48	0.33
Tl ₆ Cl ₄ S	Γ_q	7.13	0.49	1.46
Tl ₆ I ₄ S	Γ_q	7.25	0.46	1.61
TlCu ₄ S ₃	Γ_q	6.51	0.28	0.56
Ag ₂ HgI ₄	$\Gamma_{q,v}$	6.09	0.29	0.90
AgTlI ₂	$\Gamma_{q,v}$	7.06	0.35	1.26
Cu ₂ HgI ₄	$\Gamma_{q,v}$	6.11	0.29	0.27
CuTlSe ₂	$\Gamma_{q,v}$	7.15	0.35	0.01
HgAl ₂ S ₄	$\Gamma_{q,v}$	4.11	0.33	1.80
HgAl ₂ Se ₄	$\Gamma_{q,v}$	5.38	0.27	1.22
HgAl ₂ Te ₄	$\Gamma_{q,v}$	5.82	0.30	0.89
HgGa ₂ S ₄	$\Gamma_{q,v}$	5.00	0.29	1.40
HgGa ₂ Se ₄	$\Gamma_{q,v}$	6.19	0.25	0.47
HgI ₂	$\Gamma_{q,v}$	6.34	0.38	1.18
HgIn ₂ Se ₄	$\Gamma_{q,v}$	6.31	0.26	0.23
HgIn ₂ Te ₄	$\Gamma_{q,v}$	6.60	0.29	0.19
K ₂ HgO ₂	$\Gamma_{q,v}$	4.82	0.38	2.02
KTlCl ₄	$\Gamma_{q,v}$	3.52	0.35	2.17
NH ₄ TlCl ₄	$\Gamma_{q,v}$	3.15	0.36	3.37
Na ₆ PbO ₅	$\Gamma_{q,v}$	4.29	0.33	1.18
Pb ₄ Cl ₂ O ₄	$\Gamma_{q,v}$	8.05	0.49	2.40
Pb(MoO ₄)	$\Gamma_{q,v}$	6.83	0.39	0.03
Rb ₂ HgO ₂	$\Gamma_{q,v}$	5.54	0.34	1.88
Tl ₁₀ Hg ₃ Cl ₁₆	$\Gamma_{q,v}$	6.17	0.47	0.22
Tl ₅ Se ₂ Br	$\Gamma_{q,v}$	8.86	0.48	0.23
Tl ₅ Se ₂ I	$\Gamma_{q,v}$	8.59	0.47	0.68
Tl(AlF ₄)	$\Gamma_{q,v}$	6.03	0.41	4.10
TlAlSe ₂	$\Gamma_{q,v}$	6.18	0.37	0.30
TlF	$\Gamma_{q,v}$	8.37	0.50	1.89
TlGaTe ₂	$\Gamma_{q,v}$	7.21	0.35	0.29
TlInSe ₂	$\Gamma_{q,v}$	7.10	0.35	0.47

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