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Project Title:	**Discovering new Lead free perovskites for photovoltaic and Photocatalysis applications**	
Project Number	**IMURA0951**	
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Research Clusters:

Research Themes:

Highlight which of the Academy's CLUSTERS this project will address? *(Please nominate JUST **one**. For more information, see www.iitbmonash.org)*		**Highlight which of the Academy's Theme(s) this project will address?** *(Feel free to nominate more than one. For more information, see www.iitbmonash.org)*	
1	*Material Science/Engineering (including Nano, Metallurgy)*	***1***	*Advanced computational engineering, simulation and manufacture*
2		2	*Clean Energy*
3		3	*Water*
4		4	*Nanotechnology*
5		5	
6		6	
7		7	
		8	

The research problem

Drastic increase in global energy demands along with the depletion of finite fossil fuel energy has attracted the attention of scientific community towards the hunt for natural renewable energy sources. Solar energy can play a leading role to develop sustainable technology and bridge the gap between demand and supply. Photovoltaics and photocatalytic water splitting/CO_2 reduction are most promising technologies to convert these omnipresent inexhaustible solar energies into other forms of energy. Since the past decade, remarkable advances and development of various inorganic and organic-inorganic hybrid perovskite materials (chemical formula ABX_3, where A and B are cations, X is anion) has created tremendous interest to use these materials for wide applications.[1-3] This is due to their eye-catching properties such as tuneable band gap, high extinction coefficients, higher carrier mobilities, long charge-carrier diffusion lengths, low Wannier-Mott exciton binding energies. Among these, Lead halide perovskites have been on the forefront due to its excellent absorption ability e.g. 25 times that of silicon and GaAs (one of the leading photovoltaic absorber material) and proven to be promising candidate for photocatalysis/photovoltaics applications.[4,5] Pioneer efforts in optimizing perovskite material, including the interfacial engineering and device architecture has resulted in rapid increase in power conversion efficiency (PCE) to reach the latest record of 23.7 %[6-8] approaching the top values achieved with Cu(In, Ga) (S,Se)2, CdTe and silicon based solar cells. Such remarkable achievement of these materials in photovoltaics has further captivated a huge interest in the field of photocatalytic water splitting and CO2 reduction applications. Despite of the galvanizing properties of lead-based perovskites solar cell that leads to high PCE, it still suffers from major drawbacks such as performance degradation due to high susceptibility towards oxygen and moisture, crystal structure instability and highly toxic nature of Pb, which circumscribe the pace of commercialisation. There are two possible approaches that can be adopted to restrict the usage of lead in perovskite material either by fractional substitution or complete substitution of Pb(II) by non-hazardous metal cations such as Sn(II), Ge(II), Mn(II), Bi(III) or Sb(III) [9-13].

Why is Pb with ns^2 so useful?

$6s^2$ outermost shell of Pb electronic configuration ([Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$) mainly provides exceptional properties in lead-based perovskites materials [14-16]. In case of $CH_3NH_3PbI_3$, CH_3NH_3 and Pb displays +1 and +2 charge transfer to three Iodine ions. Thus, exhibiting band gap of 1.5 eV between unoccupied Pb p-orbital and occupied I-p orbital, leaving $6s^2$ electrons as a lone pair. Fully occupied $6s^2$ orbital of Pb^{2+} forms strong coupling with antibonding orbital of I-p which forms valence band maxima highly dispersive, giving small hole effective mass which is comparable to electron effective mass [17]. Additionally, strong spin-orbit coupling in post-transition element pushes conduction band minima downwards which results in positioning of high formation energy defect states either inside or near the band edge thus, decreases the possibility of formation of deep trap states [18]. Hence, combination of both the effects substantially increases charge carrier mobility making lead-based materials ideal for solar absorber material.

As such, to obtain Pb free perovskites, various divalent cations such as Sn(II), Ge(II) and Cu(II) have been employed to substitute Pb(II) cation in $CH_3NH_3PbX_3$[9-13]. However, none of them stood up to the mark because of several reasons such as (i) easy degradation to secondary phases (ii) low PCE (iii) poor optoelectronic properties. Another possibility that has been adopted is to replace Pb^{2+} by trivalent such as Bi^{3+} or Sb^{3+} element possessing s-lone pair electrons like Pb^{2+}. This results in conversion of ABX_3 into $A_3B_2X_9$ ranging from 0D to 2D structures having strongly bounded exciton and low carrier mobility. Alternatively, lead free double perovskites with general formula $A_2B(I)B(III)X_6$, here B(I) and B(III) are mono and trivalent cations or $AB(IV)X_6$ (here B-site is occupied by tetravalent cation and vacancy) can be considered as potential candidate in photovoltaics/photocatalysis applications. Nevertheless, $A_3B_2X_9$ and double perovskites still suffers from low PCE.[19, 20] In addition to high PCE, achieving long-term stability of the material is another key requirement. Substantial efforts have been taken along this direction. Replacing halides with chalcogenides is one of the possible ways, which is being explored recently.[21] However, high operating temperature restricts its further advancement to commercial level. In double perovskites, solar cell device performance is restricted due to in-efficient charge carrier transfer from absorber layer to hole transport layer (HTL) arising out of low lying valence band edge (below -5.6 eV, whereas HTL lies at -5.2 eV).[18, 22, 23] According to first principles calculations[24, 25], replacing Br by I in Cs_2AgBiX_6 helps to upshift the VBM by 0.3 eV and facilitates better device performance. Thus, mixing metal halides with highly stable metal chalcogenides can help to achieve both high PCE and robust stabiity. Partial replacement of halides by chalcogenide was conducted in Bi-based perovskites

($CH_3NH_3BiChX_2$, ch = S, Se) using density functional calculation. It predicts a direct band gap of 1.3 and 1.4 eV for $CH_3NH_3BiSeI_2$ and $CH_3NH_3BiSI_2$ respectively [26]. A more recent work on double perovskite $Cs_2AgBiBr_{5.8}S_{0.1}$ (Simonov group) demonstrated significant improvement in intrinsic light absorption with PCE increased to 1.9% and excellent stability against external environment (heat, light and humidity) compared to $Cs_2AgBiBr_6$ solar cell (1.3 %) [27]. These improvements in Bi based perovskites demand further investigation on the mixed chalcogenide-halide perovskites, in general.

Over the decade, high-throughput ab-initio screening of materials for numerous applications has emerged as a powerful tool to search for novel materials with desired properties.[28] Here one need to first fix some screening criteria keeping possible applications in mind, and then screen a combinatorial set of a large number of compounds to find the most promising candidates. Here, we are planning to perform a high-throughput computational screening to search for low cost lead-free chalcogenide-halide/pseudohalide (SCN^-, $SeCN^-$, CN^- and OCN^-) mixed perovskites using first principles computation. The search will cover various variants of perovskites including single, layered and double perovskites etc. Based on the simulated material's properties (band gap, absorption coefficient, mobility, efficiency), few promising ones will be promoted for different applications such as photovoltaics, photocatalysis, transparent conductor etc. The most potential candidates with the best-desired properties will then be fabricated/characterised experimentally. Post-experimental verification, we shall promote few materials for device application.

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Project aims

(i) To simulate and develop basic understanding of electronic and optical properties of a database of several unknown mixed chalcogenide-halide perovskites and hence discover new materials with promising properties.

(ii) Our screening will be based on the following parameters: stability, band gap, transition probability, position of valence band maxima and conduction band minima, electron/hole mobility, dielectric constant, absorption coefficient, exciton binding energy, exciton lifetime for different forms of perovskites (perovskites, double perovskites, layer perovskites).

(iii) Promote few promising materials to experimentalists for further characterization and hence use for device architecture.

(iv) To combine the theoretical insight obtained through density functional calculation with experimental findings to understand the impact of different electronic and material engineering strategies on material's stability and device performance for photovoltaics and photocatalyst applications.

Expected outcomes

i) *Create a materials database/genome for alloy structures and band properties. Help in down selecting suitable candidates for efficient energy conversion. Such database will save tremendous development time and costs needed in laboratories.*

ii) Discover NEW promising novel materials using first principles calculation, exhibiting desired properties required for specific applications.

iii) *The most **promising candidates** will be characterized in the lab and then quickly exploited for photovoltaic and photocatalysis applications ➔ Open NEW directions for solar harvesting and energy conversion research.*

iv) It is expected to establish a relation between chemical tuning and material property by looking at the experimental and theoretical trends.

How will the project address the Goals of the above Themes?

(*Advanced computational engineering, simulation and manufacture, Clean Energy*)

The field of photovoltaics and photocatalytic water splitting/CO2 reduction are considered to be one of the most promising sustainable technologies to produce clean energy, which are expected to replace exhaustible fossil fuel energy sources in near future. Recent breakthrough reports on PCE of lead-halide perovskites and continuous research along these lines made these materials a serious competitor of Si solar industry. However, the high toxicity of lead makes these materials unsuitable for clean energy technology. The main objective of the present proposal is to achieve lead free metal halide solar harvesting materials for photovoltaic and photocatalysis applications. To achieve this, we shall use advance computational techniques (density functional theory based first principles method) to screen a large combinatorial set of perovskite materials and come up with most optimum combination with desired properties. The most promising materials thus screened, will be synthesized experimentally and promoted for further device applications.

Capabilities and Degrees Required

Physics, Chemistry or Materials Science major. Basic courses on quantum mechanics and or solid-state physics/chemistry will be useful.

Potential Collaborators

Prof. Aswani Yella (Materials Engineering and Materials Science department)
Prof. Dinesh Kabra (Departme of Physics)