Prediction of optoelectronic properties and stability assessment of mixed-cation mixed-halide perovskite materials using artificial neural networks

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Abstract

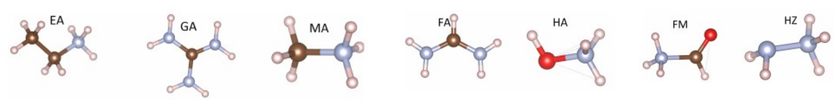
Halide perovskites are currently regarded as one of the most prominent materials for photovoltaic technology. Owing the rapid advance in photoconversion efficiency (PCE) reaching up to 25.2% and low fabrication costs, the perovskite solar cells are regarded as a strong, competing candidate for the standard silicon technology. However, further stability improvements are required, which may be achieved by using mixtures of cations and halogens, while maintaining the electronic and optical properties that ensure high PCEs. Compositional changes due to halogens (I, Br, Cl) have an impact on the stability, but also modify the electronic bandgap and, therefore, the optical absorption, being further influenced by cations with different sizes [1]. Due to the large number of possible compositions, many configurations remain unexplored. Here, we perform an analysis based on *ab initio* density functional theory calculations of perovskites containing mixtures of small-molecule organic cations and mixtures of halogens, using the SIESTA code. Several degradation mechanisms have been considered [2] for evaluating the stability. By performing structural relaxations and bond analysis, the stable 3D perovskite structures are identified. Furthermore, we employ machine learning techniques trained on the DFT output and compositional informations for the feature vectors in order to predict optoelectronic properties and formation energies associated with the likely degradation processes.

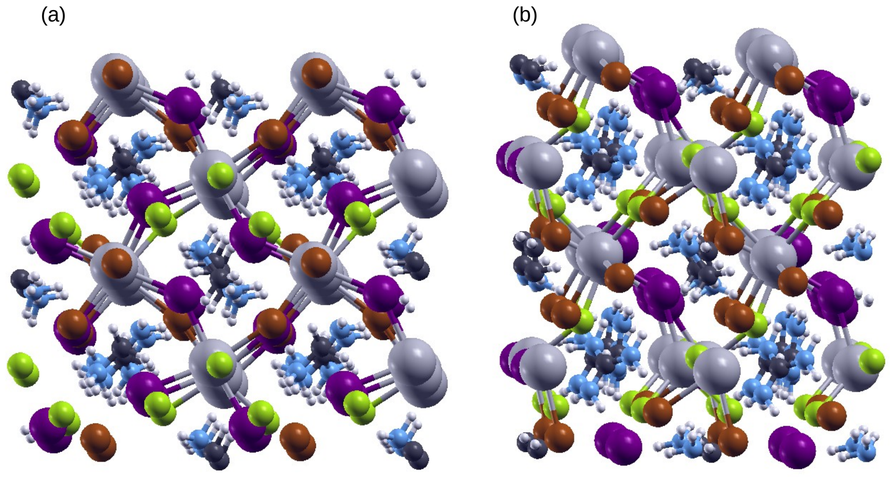
References:
[1] A.G. Tomulescu et al., Sol. Energy Mater. Sol. Cells 227, 111096 (2021)
[2] A. Senocrate et al., ACS Energy Lett. 4, 2859 (2019)

Mixed-cation mixed-halogen perovskite structures

– **7 cations:** methylammonium (MA), formamidinium (FA), ethylammonium (EA), guanidinium (GA), formamidium (FM), hydroxylammonium (HA) and hydrazinium (HZ)

– **3 halogens**: Iodine, Bromine, Chlorine





Typical perovskite mixtures: (a) MA(0.75)GA(0.25)PbI(0.33)Br(0.33)Cl(0.33) – *undistorted*
(b) MA(0.25)GA(0.75)PbI(0.33)Br(0.33)Cl(0.33) – *distorted*

In total, 1120 structures with different compositions of formula $\mathrm{A}_x\mathrm{A'}_{1-x}\mathrm{BX}_y\mathrm{X'}_z\mathrm{X''}_{3-y-z}$ have been analyzed.

Computational details

DFT calculations:

The DFT calculations are implemented using the SIESTA package, which has the advantage of linear scaling of the computational time with the system size, achieved by using strictly localized atomic numeric orbitals. For the exchange -correlation potential we employed the local desnity approximation (LDA) in the parametrization proposed by Ceperley and Alder and norm-conserving pseudopotentials by Troullier and Martins. The self-consistent solution of the Kohn-Sham equations was obtined using a double-zeta polarized basis, a mesh cutoff of 150 Ry for the real space grid and a 3x3x3 Monkhorst-Pack grid was used for the k-points sampling. The optical absorption coefficients are determined using the polycrystal model. Based on the determined total energies, the formation energies are calculated for the two degradation mechanisms.

Artificial neural networks (ANNs):

The ANNs are implemented as deep neural networks with 3 hidden layers, with Nin = 10 inputs (entity proportions, where an entity is a cation or a halogen) and Nout = 1 output, corresponding to one of the predicted quantities. The number of neurons in the hidden layers, implemented as fully connected (dense) layers, are: 100, 50, 25, 1. All neurons, except the ones in last layer use *relu* as activation function. The weights and biases are initialized as random uniform. Adam optimizer is employed with a learning rate of 10-5. The loss function is the mean squared error and accuracy is measured by the statistical coefficient of determination R2.

The train set is formed by 100 structures, which is less than 10% from the entire set (1120 structures).

Optical and stability indicators

(1) Integral optical absorption using solar spectrum (AM1.5G) for a thickness d of the absorber:

$$\Phi(d) = \int d\lambda \tilde{\Phi}_0(\lambda) \exp^{-\alpha(\lambda)d} = \int d\lambda \frac{\mathcal{S}I(\lambda)}{E_\lambda} \exp^{-\alpha(\lambda)d}$$

(2) Intrinsic degradation mechanism (decomposition to gaseous phases HX, A+A' and solid PbI_2):

$$\mathrm{A}_x\mathrm{A'}_{1-x}\mathrm{PbX}_y\mathrm{X'}_z\mathrm{X''}_{3-y-z} \rightarrow x\tilde{\mathrm{A}} + (1-x)\tilde{\mathrm{A}}' + \frac{y}{3}(\mathrm{HX} + \mathrm{PbX}_2) + \frac{z}{3}(\mathrm{HX'} + \mathrm{PbX'}_2) + \frac{3-y-z}{3}(\mathrm{HX''} + \mathrm{PbX''}_2)$$

(3) Extrinsic degradation mechanism (decomposition in the presence of O_2):

$$\mathrm{A}_x\mathrm{A'}_{1-x}\mathrm{PbX}_y\mathrm{X'}_z\mathrm{X''}_{3-y-z} + \frac{1}{4}\mathrm{O}_2 \rightarrow x\tilde{\mathrm{A}} + (1-x)\tilde{\mathrm{A}}' + \frac{1}{2}\mathrm{H}_2\mathrm{O} + \frac{y}{3}\left(\frac{1}{2}\mathrm{X}_2 + \mathrm{PbX}_2\right) + \frac{z}{3}\left(\frac{1}{2}\mathrm{X'}_2 + \mathrm{PbX'}_2\right) + \frac{3-y-z}{3}\left(\frac{1}{2}\mathrm{X''}_2 + \mathrm{PbX''}_2\right)$$

Absorption and stability indices – definitions:

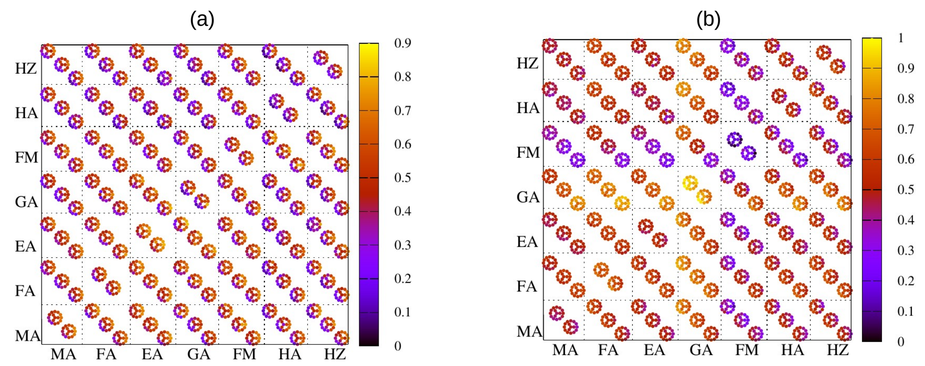
$$f_\mathrm{a}(d) = (\Phi(0) - \Phi(d))/\Phi(0)$$

$$f_\mathrm{s}^{(i/e)} = (E_\mathrm{f}^{(i/e)} - E_\mathrm{f}^{\min})/(E_\mathrm{f}^{\max} - E_\mathrm{f}^{\min})$$

$$E_\mathrm{f}^{(i)} = \sum_i x_{\mathrm{p_i}}^{(i)} E_{\mathrm{p_i}}^{(i)} - E_\mathrm{prv}$$

$$E_\mathrm{f}^{(e)} = \sum_i x_{\mathrm{p_i}}^{(e)} E_{\mathrm{p_i}}^{(e)} - E_\mathrm{prv} - \frac{1}{4}E_{\mathrm{O_2}}$$

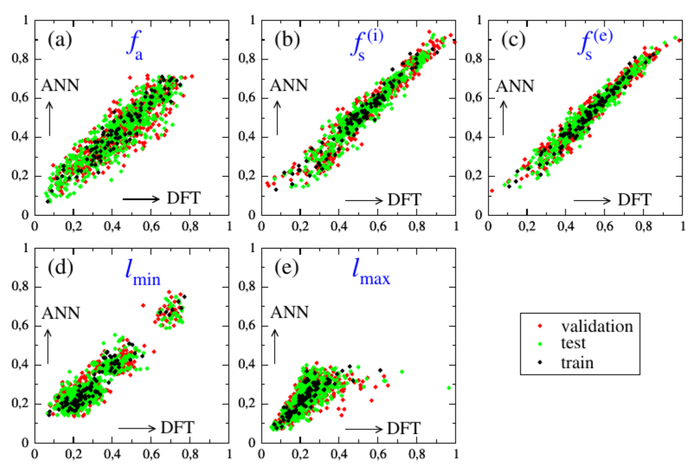
Optical performance and chemical stability (*)



(a) Optical performance measured by the f_a index: iodine based systems have the smallest gap (large absorption), followed by bromine and chlorine with the largest gaps (small absorption). Mixtures have intermediate behaviors. EA and GA based perovskites indicate the best absorption properties.
(b) Stability indices (f_s) for the intrinsic (upper-left triangle) and extrinsic (lower-right triangle) degradation mechanisms, respectively:
- Compounds based on GA, FA and Br are most stable for the intrinsic mechanism;
- Compounds based on GA, FA and Cl sre most stable for the extrinsic mechanism;
- Compounds based on FM are least stable, followed by HA and HZ.

(*) The rows correspond to A cations, while the columns are index by A' . We used the following convention: each matrix element contains three binary mixtures of cations (three composite circles, each with 16 dots, corresponding to different proportions A - A' (25%-75%, 50%-50%, 75%-25%), three binary halogen mixtures (dots on the circles) with the same proportions as A-A' and four ternary halogen mixtures of type 50%-25%-25% (dots within the circles). The middle dot corresponds to equal halogen proportions.

Prediction of optical and stability performance indicators using ANN models



The accuracies of the ANN models, measured by R2, during training (black), validation (red) and test (green), for the absorption and stability indices, as well as for the minimum and maximum Pb-X bond lengths. The R2 coefficients are: (a) 0.82; (b) 0.92; (c) 0.95; (d) 0.84; (e) 0.43.

Conclusions

We investigated the optical absorption and stability properties of mixed-cation mixed-halogen perovskites using high throughput DFT calculations. Defining optical absorption and stability indices, the most promising candidates are identified: mixtures based on EA-GA, FA-GA are most stable, whereas EA-GA and EA-FA indicate high absorption. One of best ranked candidates from both perspectives is $EA_{0.25}\ GA_{0.75}PbI_3$ (f_a=0.81 and f_s=0.77). Highest stability is obtained for $GAPbBr_{2.25}Cl_{0.75}$ (f_a=0.26 and f_s=0.94), with a diminished optical performance, which points out the double role of lighter halogens. We show that it is feasible to achieve reasonable accuracies for predicting absorption and stability indices using ANN models, which are trained on a significantly smaller sub-set (<10%).

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