процесса синтеза полимеров и получения продуктов с нужными характеристиками молекулярной массы.

В целом, гель-проникающая хроматография является хорошим инструментом для анализа молекулярных масс и структур полимеров, что может иметь важные практические применения в различных областях, таких как материаловедение, биотехнология и фармацевтика.

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EFFECT OF CATION SUBSTITUTION IN THE STRUCTURE OF HALIDE PEROVSKITES ON THEIR STRUCTURE BASED ON THE CALCULATION OF THE DENSITY FUNCTIONAL AND MOLECULAR DYNAMICS

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The impressive photovoltaic performance of perovskites has made them one of the most promising high-efficiency photovoltaic materials. The study of this type of solar elements is relevant for Central Asia region. Toward to advance of perovskite applications in solar cells, a wide range of surface passivation strategies have been developed using a large variety of organic and inorganic molecules for Lead-halide (and other some metals) perovskites as well as thin films [1,2]. In perovskite crystal structure, such in classical semiconductors, two of the main classes of defects are point defects (atomic-scale) and structural defects.

In this work, we present a theoretical investigate the statistic and dynamic properties of partially substituted halide perovskites in which methylammonium (MA) are partially substituted by organic cations by means of first-principles DFT and molecular dynamics calculations. Here we mainly focus on suppression effect of diffusion of organic cations an effect of partially substituted perovskites (of

suppression effect of diffusion of A position ions (MA or X)) on their bandgaps, structural parameters, and the diffusivity of cations, which would provide clue for defect passivation on their structure. In our calculations, we considered the Tkatchenko-Scheffler method with regular Hirshfeld partitioning (TS) was considered as a semi empirical dispersion-correction. The lattice parameters of the optimized super cell from the calculation without dispersion correction were a = 12.86 Å, b = 12.87 Å, and c = 13.02 Å with the volume of 2147 $Å^3$. The calculation with dispersion correction of the lattice parameters of the optimized structure from were a = 12.65 Å, b = 12.67 Å and c = 12.81 Å with the cell volume of 2055 $Å^3$. The calculation with dispersion correction gives acceptable lattice parameters those are closer to the initial cubic lattice of a = 12.66 Å. We considered in the all-following calculations TS dispersion correction and the calculated bandgap with considering dispersion force is close to the experimental value of 1.55 eV [3].

We partially replaced the organic cation in $MAPbI_3$ structure with the different cation substituents. We have inserted 8 cations as substituents into the perovskite unit cell with maintaining 8 molecules of MA at their initial position. Because the lamellar distribution will introduce large structural distortions compared to randomly substituted structures, in this study, eight molecules were substituted for those located at the ab-axis plane. The results is noted the cell volumes of partially substituted perovskite increases with the increase in the ionic radius of substituted organic molecules compare to that of un-substituted perovskite. The tendency of the cell volume is different for Cs^+ because has a unique interaction with the framework compared to the interaction of organic cations inorganic substituent. The lattice angles of partial substitution perovskites slightly differ, it is noted that most distorted structure is $MA_{0.5}(NH_2NH_3^+)_{0.5}PbI_3$ of which the bandgap of is the smallest among other cations. The partial substitution of perovskite can vary a space within the perovskite framework, which would change mobility of ions at A position.

Figure 1(a) shows partial density of states (PDOS) of the $MAPbI_3$, the valence and conduction bands consist mostly of the I 5p and Pb 6p orbitals, respectively, which is consistent with report [4], and (b–f) show the PDOS with most significant differences in the electronic structures of partially substituted perovskites. Calculation results are no significant differences in the electronic structures between partially substituted perovskite structures. The organic cation acts as a charge compensating center but does not participate in the frontier electronic and band structure [5,6], that is true for our calculations. But the calculated band gap of partially substituted perovskites, are slightly smaller than that of unsubstituted perovskite.

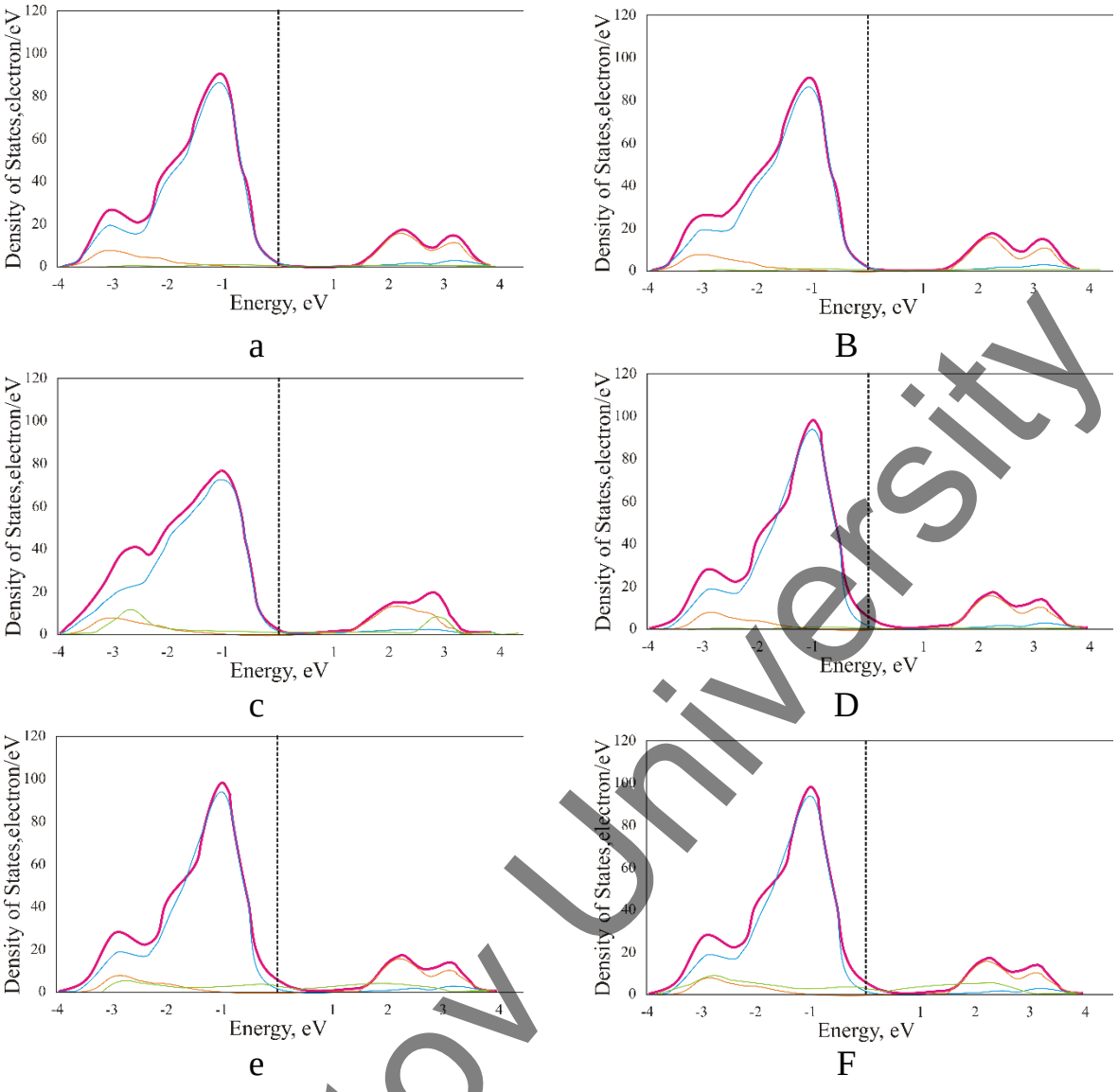

Figure 1. Calculated partial density of states (PDOS) of (a) $CH_3NH_3PbI_3$, partially substituted $MAPbI_3$ by: (b) $(NH_2)_2CH^+$, (c) $(CH_3)_2NH_2^+$ (d) Cs^+, (e)$CH_3CH_2NH_3^+$, (f) $NH_2NH_3^+$. Where color is: Total, I 5p, Pb 6p, Organic cation.

The vacancy migrations and lattice distortion is most dominant processes for for halide perovskites [7]. MD simulation using the partially substituted perovskite structure was conducted to investigate the effect of a lattice distortion on ionic mobility. By using MD calculations we have demonstrated (Figure 2) the snapshots of the structure of the unit cell of $MA_{0.5}((NH_2)_2CH^+)_{0.5}PbI_3$. The rotation of two cations between A positions is clearly indicated with maintaining perovskite the Pb−I framework is distorted with longer Pb−I bonds. This results in the formation of local distortions that can be characterized as short-range order without long-range order. Calculation results is noted that although the size of the unit cell of partially substituted perovskite by $(NH_2)_2CH^+$ cation shrunk compared to the $MAPbI_3$, but the averaged diffusion coefficient in substituted perovskiteincreases compared to that for

un-substituted one. This effect is because the unique cation of $(NH_2)_2CH^+$ with bandgap of 1.44 eV promotes a migration by prompt supplying vacancy for MA migration. The calculated diffusion coefficient of MA in $MA_{0.5}Cs_{0.5}PbI_3$ significantly increases compared to that of unsubstituted perovskite. This fact is because the distortion of the unit cell of perovskite resulting in extending the diffusion length promotes the migration of MA cations. The diffusivities of all cations in substituted perovskites are smaller than those in $MAPbI_3$ and also in other substituted perovskites. We think this would be because of the effect of distortion of the perovskite lattice, where larger cations inhibit diffusion of MA while a distortion caused by the mismatch of lattice suppress diffusion of larger cations.

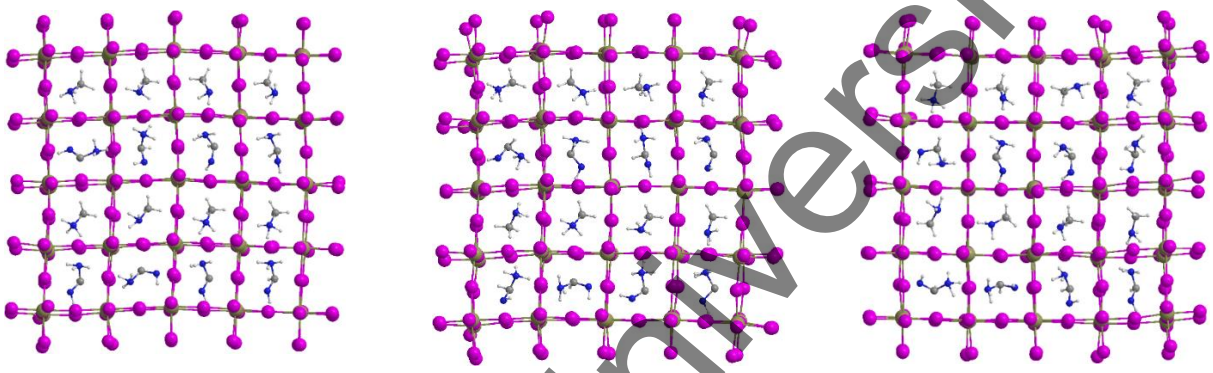

Figure 2. The snapshots of the unit cell obtained from MD
for $MA_{0.5}((NH_2)_2CH^+)_{0.5}PbI_3$ at different time

In this work, we have performed a molecular dynamic simulation and DFT study the structural, electronic and ionic diffusivities of the partially substituted cubic $MA_{0.5}X_{0.5}PbI_3$ with different sized A-site cations. The electronic structure analysis indicated that calculated bandgaps of the investigated partially substituted perovskite are decreased with increasing the substituted cation size and slightly lower for all the cases compared to the $MAPbI_3$ perovskite. According to MD results show that the mobility of the averaged cations in partially substituted unit cells depends on the size of cations. The diffusivities of cations in partially $NH_2NH_3^+$ substituted $MAPbI_3$ is significantly suppressed comparing to that of un-substituted and also the other substituted systems. The simulation results show strong agreement, indicating that all the cation substitutions increase the activation energy for iodide ion transport relative to pure $MAPbI_3$.We show that just 25% MA substitution strongly suppresses iodide ion transport, with no observable ion diffusion in the timescale of our measurements. This computational study enhances our fundamental understanding of mixed-cation perovskites, and provides a design strategy for reducing iodide ion transport that has important implications for improving solar cell performance.

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КОМПОНЕНТНЫЙ СОСТАВ ЭФИРНЫХ МАСЕЛ НЕКОТОРЫХ ВИДОВ РАСТЕНИЙ РОДА *ACHILLEA* L

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Расширение арсенала официнальных эфирномасличных растений является актуальной проблемой фитохимии. Состав и количественное содержаниекомпонентов эфирных масел во многом определяют биологическую активность растительного сырья.

Виды растений рода тысячелистник (*Achillea* L.) рассматриваются как перспективный источник биологически активных веществ, среди которых наиболее важными являются терпеноиды. Препараты на основе тысячелистника