Molecular-dynamics modeling of structural stability of MAPbX3 (X=I-, CL-, BR-) as solar cells elements

M. Husenzoda ^a, L. Gahramanli ^{bc*}

^a Tajik Technical University named after academician M.S. Osimi, Dushanbe, 734042, Tajikistan

^b INFN - Frascati National Laboratories, E. Fermi Street 54, Frascati, 1-00044, Italy

^c Baku State University, 23 Academic Zahid Khalilov Street, Baku, AZ1148, Azerbaijan

The methods for forming hybrid organo-inorganic perovskite structures in the form of thin films and their stability are studied. The molecular-dynamics (MD) simulation approach was used to conduct theoretical analyses of materials based on the hybrid organo-inorganic perovskites MAPbX3. The classical perovskite structures based on CaTiO₃ are considered the basic structure to refine the methodology of computer simulation and optimize the shape and parameters of the interaction of atomic potentials. Series of MD calculations with various model concepts, and models of flexible and rigid coupling of perovskites, the heating process's influence on the structure has been analyzed in a wide range.

(Received October 16, 2023; Accepted January 4, 2024)

Keywords: Hybrid organo-inorganic perovskites, Photoelectric converters, Adsorber, Molecular dynamics, Radial distribution function, X-ray structural analysis

1. Introduction

For the time being, constant advancements in semiconductor nanomaterials are promising and essential in creating photovoltaic structures. Permanent material production is a significant activity of modern nanotechnology, for example, in the development of technically advanced optoelectronic devices, display equipment, LEDs, and solar electricity equipment, among other things. In this regard, computer modeling and simulation of nanostructures to develop new types of solar cells and increase their performance are important topics in science. Methodsbased on computational atomic and molecular methods can be used to learn about the crystal chemistry of semiconductor materials used in solar cells and the dynamic, structural, and thermodynamic properties of phase transitions, diffusion processes, charge transfer, etc. One type of these materials is hybrid organic-inorganic perovskites (HOIP). Crystalline materials with the perovskite structure with general formula ABX₃ (where X are anions O^2 , \overline{F} , \overline{Cl} , \overline{Br} , and \overline{I}) are widely used in engineering due to acombination of unique electrical and photovoltaic properties, such as magnetoelectric, piezoelectric, dielectric, semiconductor, and catalytic activity. Currently, efficiency of hybrid organic-inorganic solar cells exceeds 20%. Perovskite solar cells are less efficient than crystalline silicon cells, but their manufacturing technology is simpler and cheaper. According to experts, perovskite materials are expected to hold more promise in the production of solar cells as an alternative to silicon. Hybrid organic-inorganic halide perovskites, in which the monovalent cation is an organic nitrogen base cation, have a large optical absorption coefficient and unusually high electron and hole mobility, allowing them to be among the leaders of modern photovoltaics [1-6].

^{*} Corresponding author: gahraman.lala@gmail.com https://doi.org/10.15251/JOR.2024.201.21

2. Materials and methods

2.1. Hybrid organo-inorganic perovskites (HOIP).

In 1978, Weber was the first to discover the structure and physical properties of HOIP [7]. Interest in HOIP continues to grow due to its attractive properties, which include low material cost, ease of synthesis, suitable bandgap, ultrafast carrier generation [8], the slow recombination rate of electron-hole carriers [7], low-temperature processing (~120 °C) [9], a large diffusion length of electrons and holes [10], a rather long lifetime of nonequilibrium charge carriers (up to 1 μ s), excellent thermal stability and a small exciton binding energy [19–50 meV] [11].

Crystalline materials have a perovskite structure with the general formula ABX₃ in which the metal cation "A" is occupied by a monovalent organic (for example, CH_3NH^+ , $CH(NH_2)_2$, $(NH_2)_3C^+$ or inorganic (for example, K^+ , Rb^+ , Cs^-) cation, at sites "B" divalent metal cations such as Pb⁺, Sn⁺, Ge⁺, Mg⁺, Ca⁺, Sr⁺, Ba⁺, Cu⁺, Fe⁺, and Eu⁺ and at the "X" sites the halide ion (Cl⁻, Br⁻, I⁻). The crystal structure of HOIP is depicted in Figure 1.



Fig. 1. Crystal structure ABX₃.

Low-temperature wet methods (spin-coating, drop-casting, dip coating, doctor blading, screen-printing, and spray methods) are used most commonly to synthesize perovskite materials [8]. There are two types of solution-based MAPbI₃ thin film synthesis methods: one-stage and two-stage. In a one-step method, perovskite structures are generated by combining methylammonium iodide (MAI) precursors and lead iodide PbI_2 in one solvent. In the two-step method, sequential precipitation of methylammonium iodide (MAI) and lead iodide PbI_2 from precursors occurs in solutions.

The first one is the simplest and most widely used process. The second one specializes in optimizing the perovskite film to improve crystallinity, morphology, and homogeneity [6-11].

To obtain a perovskite structure, aprotic solvents such as γ -butyrolactone (GBL), N, Ndimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and N- methyl pyrrolidone (NMP) are added to the substrate by spin-coating.

The formation of the perovskite film occurs in two main stages: removing the excess solvent by evaporation and the crystallization of the solid perovskite film. In the classical one-step method, these two steps, as a rule, occur simultaneously during the deposition and/or in the subsequent annealing process.

Two methods are commonly used to deposit high-quality perovskite films using the singlestage method:(1) a smooth precursor film is formed, and then perovskite is formed during the slow crystallization process (2) perovskite films are obtained directly by accelerating perovskite nucleation, i.e., the crystallization process occurs even before the solvent evaporates [12].

The main disadvantage of the one-step method is that the perovskite films produced have poor morphology and crystallinity. The main precursor PbI₂, on the other hand, can be conveniently

"packed" in a uniform, compact film using "wet" methods [8].

A layer of PbI_2 is usually applied in the first stage of the two-step process [13], which is then converted to MAPbI₃ by intercalation with MAI.

This method has two main features: (1) the morphology of the final perovskite film is largely determined by the PbI_2 film, and (2) the reaction rate is determined by the diffusion of CH_3NH_3I into the PbI_2 lattice.

A warm substrate and a slightly heated (60–70°C) PbI₂ precursor solution are typically used to obtain a smooth perovskite film. Spin-coating is used to ensure uniform deposition of PbI₂ film on a substrate. The expansion of the PbI₂ film volume during the intercalation of MAI is the crucial problem with the two-stage process [14].

2.1. Degradation of hybrid organo-inorganic materials.

One of the issues with HONP based on the classical structure of $CH_3NH_3PbI_3$ is that the material degrades when exposed to moisture in the air. Frost J. M *et al.* The scientific literature [15], presents a potential mechanism for the decomposition of the perovskite structure of methylammonium lead triiodide in the presence of water as shown in Figure 2. When $CH_3NH_3PbI_3$ interacts with water, it decomposes into CH_3NH_2 ,PbI₃, and HI occurs [15]. In addition, these materials are subject to thermal decomposition into ammonia NH_3 and methyl iodide CH_3I at relatively low temperatures compared with conventional inorganic semiconductor materials.



Fig. 2. Possible decomposition path of hybrid halide perovskites in the presence of water. The water molecule (a) is necessary for initiating the decomposition process caused by phase transformations of both hydrogen iodide (b) and methylammonium (c) and (d) water molecule and lead iodide.

To address the issue of degradation in hybrid organo-inorganic perovskite products, researchers are working on substituting the organic cation (MA, methylammonium cation) with organic and inorganic cations [16-18], which are resistant to the environment. The formation of new semiconductor materials with a perovskite structure requires a more detailed study of properties. In developing high-performance solar cells based on novel HOIPs, it is important to rely on the results of theoretical studies of their properties. Both the MD method and molecular modeling are used to study the properties of elementary constituents of complex nano- and molecular structures and design organic compounds that make up other chemicals. MD simulation allows for studying the melting and phase transition processes, diffusion, conductivity, etc. The application of the MD method significantly reduces the time and cost of conducting the experimental part since the structure of new materials can be predicted using the method. ByMD and quantum-chemical calculations, it is possible to predict the properties of new perovskite complexes and the possibility of their introduction into new photovoltaic systems [19].

It's worth noting that computational methods are crucial for studying systems and molecules' physical and chemical properties. On the one hand, such techniques are used to confirm experimental results. On the other, they are used to explore novel ways to test experimental findings [20-25].

3. Results and discussions

3.1. Structural properties of CaTiO₃

As a first step, MD modeling of the basic structure of calcium titanateCaTiO₃ (Ca²⁺⁷,

 Ti^{4+} , O^{2-}) was carried out to study the modern HOIP structures of the type ABX₃ to develop the procedure for a computer-assisted MD studyand optimization of the form and parameters of interatomic potentials.

A typical representative of the class of modern perovskite materials is calcium titanate CaTiO₃. The mineral was discovered in the Ural Mountains of Rossi by Gustav Rose in 1839 [26] and was named after the Russian mineralogist Lev Alekseevich Perovsky. Later, the term "perovskite" was borrowed to describe any material with the same type of crystal structure as calcium oxide, called the perovskite structure.

The general chemical formula for pure perovskite compounds is ABX₃,where "A" and "B" are two cations of different sizes, and "X" is an anion that is associated with both. They have a valence ratio of 1:2:1. Figure 3 shows the cubic structure of the usual perovskite composition ABO₃ (cation A is larger than cation B). In these perovskites, the cation A represents a 2 valent metal $(Mg^{2+}_{4}, Ca^{2+}_{4}, Sr^{2+}_{4}, Ba^{2+}_{4}, Pb^{2+}_{4})$ in the center of the lattice element there is a 4 valent cation B (Ti⁴⁺, Si⁴⁺, Mn⁴⁺, Fe⁴⁺) around the cation A. There are oxygen anions (O²⁻) [27].



Fig. 3. ABO₃ perovskite structure: (a) corner-sharing octahedra with ions A located in 12-coordinated interstices, (b) cation B sites in the center of the lattice.

Previously, we carried out the preliminary MD study of the crystal structure of CaTiO₃ [1]. The research was carried out to investigate the dynamic and structural properties of the perovskite CaTiO₃, analyzing the effect of the type of potential functions on the structural equilibrium properties of the perovskite, surveying the structural characteristics of perovskites, and new MD analysis data [28-32]. Notably, perovskite inorganic materials are crystals with ion-covalent or ionic bonds [30]. Despite the partially covalent nature of the Ti–O bond, the system is simulated based on the pair interaction with the central power and the interatomic potential of the VR type. The VR interatomic potential was successfully used to study many different systems [30]:

$$U = \sum_{i < j} U_{ij} U = \frac{z_i Z_i e^2}{r} \cdot e^{\frac{r}{\lambda}} + \frac{H_{ij}}{r^{\eta_{ij}}} - \frac{D_{ij}}{2r^4} \cdot e^{\frac{r}{\xi}} - \frac{W_{ij}}{r^6}$$
(1)

The first term in equation 1 is the Coulomb interaction potential between ions Z_i and Z_j (in units of electron charge |e|), $r_{ij} = r_i - r_j$ is the distance between the *i* and *j* ions, and the λ parameter is the scanning length of the Coulomb forces. The second term represents the steric repulsion and includes the repulsion effects due toionic sizes, where H_{ij} and η_{ij} are the strength and the exponential

index of the steric repulsion, respectively [9], with η_{ij} values of 11 for the Ca–Ca and Ti–Ti atomic pairs, 9 for the Ca–Ca and Ti–O pairs and 7 for the O–O pairs). The third term is the charge-induced dipole-dipole interaction, which takes into account the electronic polarizability of the atoms, and D_{ij} is the gravity force of dipole charge (O₂ is known to be a strongly polarizable ion). The last term is the induced dipole-dipole potential of the van der Waals type, where W_{ij} is the interaction degree. The parameter ξ is the shielding length for the charge-dipole interactions.

In this paper, we neglect the scanning condition (screening) for the Coulomb (i.e. $\exp(-r/\lambda) = 1$) and charge-dipole ($\xi \rightarrow 0$) interactions. In addition, to simulate the spatial repulsion of ions, we consider the fixed value $\eta_{ij} = 12$ for all interacting atom pairs. In this approximation, as mentioned above, the VR interatomic potential is close to the well-known Lennard-Jones (LJ) potential or the(12-6) type, which is widely used for the MD simulation of condensed molecular systems such as perovskites [14–19]. The MD calculation was performed for a system of 16,000 particles (3200 Ca + 3200 Ti + 9600 O), initially set in the *Pbnm* orthorhombic structure. The initial structure was built using the Institute of Experimental Mineralogy database of the Russian Academy of Sciences, (CardNo: 3594, PEROVSKITE CaTiO(3), Orthorhombic Pbnm, Z = 4; Unit cell parameters: a = 5.37 A, $\alpha = 90^{\circ}$; b = 5.44 A, $\beta = 90^{\circ}$; c = 7.64 A, $\gamma = 90^{\circ}$; unit cell volume V = 223.19 Å³; molar volume $V\mu = 33.61$ cm³/mol. The size of the orthorhombic MD cell was Lx = 43.022 A, Ly = 43.494 A, and Lz = 61.107 A, which provided the density corresponding to the experimental value $\rho = 4$ g/cm⁻ as reported in [30]. When the suggested interatomic potential was used, the initial state of the structure of the MD system was stabilized in its equilibrium configuration at room temperature. According to the MD method, calculations were performed based on the DL POLY multi-purpose computer code [1,33]. The equilibrium configuration and pair distribution function of the CaTiO₃ perovskite structure were presented based on the obtained data.

3.2. Equilibrium configurations and radial distribution function

The perovskite structure is changed during the relaxation process, and the sample is recrystallized due to melting and cooling processes. Recrystallization in single crystal is well known to occur in an orthorhombic structure, thoughamorphous regions produced immediately during relaxation are also present. These results obtained via MD calculation are correlated with previous experimental and simulation data for a polycrystalline material with a structure similar to perovskite CaTiO₃ [1]. Figures 4a and 4b show computer-generated structures of perovskite CaTiO₃ in their initial state and after the relaxation of the system (in an equilibrium state).



Fig. 4. Computer-generated perovskite structures of CaTiO₃: (a) the initial structure and (b) the structure after relaxation

The radial distribution function (RDF) $g_{\alpha\beta}(r)$ is shown in Figures 5–7. For comparison, we also present the results obtained by González-Vázquez J. P. *et al.* [9] using the VR potential. Figure 5 shows RDF plots $g_{\alpha\beta}(r)$ for the Ca–Ca ion pair using the (12-6) potential (a) and the VR potential

(b) [1]. It is seen that the behavior of RDF is similar for both the (12-6) and VR models. Three large $g\alpha\beta(r)$ peaks are observed for each model. The positions of $g\alpha\beta(r)$ peaks in the case of (12-6) potential are closer to the origin of the coordinate axis *r*. So, the (12-6) model suggests a stronger bond in the Ca–Ca ion pair as compared with the VR model. In Figure 6, the RDF plots have shown the Ca–O ion pair. A comparison [9] shows that the positions of the $g\alpha\beta(r)$ peaks for both (12-6) and VR potentials are very close to each other. A significantly higher $g\alpha\beta(r)$ is observed for the (12-6) potential: the value of the $g\alpha\beta(r)$ peak in the model (a) is four times thatin the model (b). This means that the Ca–O pairs have a strong ionic correlation for the (12-6) potential rather than for the VR one. Figure 7 presents RDF plots for the O–O ion pair. The $g\alpha\beta(r)$ amplitude for both (12-6) and VR potentials are similar. Nevertheless, the secondary peak $g\alpha\beta(r)$ appears in model (a) (with 12-6), which is not present in model (b) (with VR). Thus, even though O₂ is also a very polarizable ion, the neglect of the contribution of the Coulomb and charge-dipole interactions for the O-O pairwise interaction does not affect the O-O ordering.



Fig. 5. RDF $ga\beta(r)$, where r is the radius of the Ca–Ca ion pair at T = 300 K, obtained by MD using (a) the (12-6) potential and the VR potential.



Fig. 6. RDF $ga\beta(r)$, where r is the radius of the Ca–O ion pair at T = 300 K, obtained by MD using (a) the (12-6) potential and (b) the VR potential.



Fig. 7. RDF $ga\beta(r)$, where r is the radius of the O–O ion pair at T = 300 K, obtained by MD using (a) the (12-6) potential and (b) the VR potential

3.3. The study of the perovskite structure CH₃NH₃PbCl₃ by the method of molecular dynamic modeling (MD) and X-ray structural analysis (XRD)

The method of MD modeling is very convenient for studying the stability of the structure of various materials and biomolecular systems, resulting from changes in temperature or pressure.

Zelenyak T.Yu. et all. [34] described indetail the methodology for conducting a theoretical study of the effect of theheating process on the perovskite structure $CN^{+}Pb^{2+}Cl_{3}^{-}$ ($CN^{+} \equiv CH_{3} NH_{3}^{+}$) in a wide temperature range from 300 K to 1000 K. Figure 8 shows a series of MD calculations were carried out for models of flexible and rigid bonds, where data of structural modifications of the perovskite $CN^{+}Pb^{2+}Cl_{3}^{-}$ are obtained using the RDF.



Fig. 8. Model of rigid and soft chemical bonding in the unit cell of perovskite CH3NH3PbCl3: (a) rigid bond model and (b) soft bond model.

Comparative characterization of pairwise ion-ion correlations in the perovskite system CH₃NH₃PbCl₃ in terms of the rigid and soft bond models was carried out. The temperature dependences of the RDF for different ion pairs are shown in Figures 9a–9d.



Fig. 9. Radial distribution functions of different ion pairs according to MD simulation data for the models of rigid and soft chemical bonds in the unit cell of perovskite CH₃NH₃PbCl₃: (a) CN–CN, (b) CN–Pb (c) CN–Cl, and (d) Pb–Cl.

The RDF plays a central role in molecular modeling; it can be calculated from experiments to determine the structure of substances (X-ray diffraction and neutron diffraction). Table 1 sums up the results of MD simulations of the action of the RDF, $g_{\alpha\beta}(r)$, for interacting ion pairs CN–CN

 $(CN^+ \equiv CH_3NH_3)$ for the soft and rigid bond models.

The study of crystals gives the most information about the crystalline composition of the substance. By obtaining X-rays, you can set the crystalline composition of the substance, that is, to conduct a phase analysis. So, for a complete study of the determination of the structure of a substance, XRD is used.

XRD is the main method for determining the structure of crystals. This is because the crystals have a strict periodicity of the structure and are a diffraction grating created by nature itself for XRD. The crystal structure of the complex of lead methyl ammonium trihalide with the formula ABX_3 (A= CH₃NH₃⁺, B = Pb²⁺, Sn²⁺, X = Cl⁻, Br⁻, or l⁻) was studied using XRD [2].

	Pairwisbonds Bond model		Temperature, T = 300 K		Temperature, T=1000 K		
			Crystal lattice packing probability, Å	g(r) max	Crystal Lattice Packing probability,Å	g(r) max	
CN-C	N	Soft	[4.0 - 7.0]	1,7	[3.8-7.2]	1,5	
		Rigid	[4.0 - 5.0]	1,2	[3.0 - 5.3]	1,1	
CN-P	b	Soft	[4.0 - 5.0]	5.6	[3.8-5.2]	3.1	
		Rigid	[2.8 - 6.2]	2.4	[2.8 - 6.0]	1.5	
CN-C	1	Soft	[3.4 - 5.0]	9.0	[3.4 - 5.0]	4.9	
		Rigid	[3.0 - 5.0]	2.6	[3.0 - 5.0]	3.0	
Pb-Cl		Soft	[2.4 - 2.8]	9.0	[2.4 - 2.8]	>10	
		Rigid	[2.0-2.6]	>10	[2.0 - 2.6]	>10	

Table 1. MD calculation data for the behavior of RDF of the perovskite model $CN^+ Pb^{2+} Cl^{3-} (CN^+ \equiv CH_3NH_3^+)$ at temperatures of 300 K and 1000 K [1].

The heating of the structure leads to a phase transition and, at the same time, to a distortion of the crystal lattice. In the cubic symmetry, the $CH_3NH_3^+$ ion is polar and has the C_{3v} -symmetry, which can contribute to the disordering of the cubic phase, but the cubic phase also contains the disordered halogen as shown in Figure 10a. The site occupancy was set at 1/4 for I and 1/12 for C and N. With decreasing temperature, the cubic phase transforms into the tetragonal phase, as shown in Figure 10b. The Γ ions are ordered for the tetragonal phase, thereby leading to a lower symmetry category from the cubic phase. The site occupancy was set at 1/4 for C and N for the tetragonal structure of $CH_3NH_3PbI_3$. As the temperature decreases, the tetragonal phase transforms into the

orthorhombic phasedue to the ordering of the CH₃NH['] ions in the unit cell, as shown in Figure 10c.



Fig. 10. Crystal structures of CH₃NH₃PbI₃: (a) cubic, (b) tetragonal, and (c) orthorhombic.

For a broader representation, the perovskite systems $CH_3NH_3PbCl_3$ and $CH_3NH_3PbBr_3$ were additionally studied. The structural parameters and the interatomic distance of the perovskite systems $CH_3NH_3PbX_3$, where X = Cl, Br, or I, are presented in Table 2.

Wang *et al.* [35] considered the influence of temperature on the bandgap of CH₃NH₃PbI₃. In the CH₃NH₃PbI₃ structure, the Pb–I bond length greatly depends on the thermodynamic motion of the organic base. The bandgap value depends strongly on the heating temperature.

Pairwisebonds	The crystal lattice of CH ₃ NH ₃ PbX ₃	Interatomic distance, Å	Т(К)	Space group, Å			Occupancy factor
	(X=Cl, Br, and I)	,		Α	В	С	
	Cubic CH ₃ NH ₃ PbI ₃		330	Pmm (Z	=1)		
				6,391			
Pb-I		5.0					
C-N		2.3					
-	Tetragonal CH ₃ NH ₃ PbI ₃		220	14/mcm (Z=4)			
				8,800		12,685	
Pb-I(1)		3.6					
Pb-I(2)		2.5					
C-N		1.5					
	Orthorhombic		100	Pnma (Z=4)			1.0
	CH ₃ NH ₃ PbI ₃			8.8362	12.5804	8.5551	
Pb-I(1)		2.6					
Pb-I(2)		3.6					
C-N		5.0					
	Cubic CH ₃ NH ₃ PbCl ₃		200	Pm3m (2	Z=1)		
				5.666			
Pb-Cl		5.0					
C-N		2.4					
	Cubic CH ₃ NH ₃ PbBr ₃		298	Pm3m (2	Z=1)		
				5,933			
Pb-Br		4.7				1	
C-N		5.7					

Table 2. Structural parameters of CH₃NH₃PbX₃ at temperatures of 100, 200, and 330 K.

It was determined experimentally that there are strongly deformed PbI_6 octahedra (and, consequently, distorted Pb–I bond lengths) during a change in temperature of the cubic structure, although the lattice $CH_3NH_3^+$ parameters remain unchanged, as shown in Figure 11. Nonetheless, this temperature effect has not been fully considered in the scientific literature [35]. It is known that $CH_3NH_3PbI_3$ is sensitive to moisture and tends to decompose into PbI_2 (and $CH_3NH_2 + HI$), which has a large bandgap (2.3 eV).



*Fig. 11. Local PbI*⁶ *octahedra of the CH*₃*NH*₃*PbI*₃ *structure: (a) orthorhombic, (b) tetragonal, and (c) pseudo-cubic.* We assume that mixing the phases with PbI₂ can make an experimental contribution to the

change in the bandgap. Thus, the properties of the crystal structure must be carefully examined to calculate the bandgap.

The average lengths of the Pb–I bond in the PbI_6 octahedron are 3.18, 3.22, and 3.14 A for the orthorhombic, tetragonal, and pseudo-cubic structures, respectively. According to the presented computational findings, the MD approach has gained prominence in materials science due to its significant contributions. As recently reported in the literature [36-41], these results are well-known in many systems and molecules for a wide range of applications.

4. Conclusions

This work covers experimental and theoretical studies of HOIP systems. They were studied by the method of molecular-dynamic modeling of the classical structure of calcium titanate CaTiO₃, as the basic structure. Based on the obtained data on MD for CaTiO₃, the structure of perovskite MAPbX₃ (where X=I, Cl, or Br) was investigated by the combined methods of MD and XRD. A series of MD calculations were carried out using different model principles, including flexible and rigid perovskite coupling models. The influence of the heating processon the structure of organicinorganic perovskites has been analyzed in a wide temperature range. New data were obtained on the structure of the HOIP crystal lattice CH₃NH₃PbCl₃. They can be used as the basis for experimental measurements(X-ray structural analysis and neutron diffraction) by determining the material's structure in the amorphous (liquid-shaped) phase.

Acknowledgments

The authors express their deep gratitude to the scientific consultants, Professor of the Joint Institute for Nuclear Research Kholmurodov Kh.T. and Professor Tatyana Yu. Zelenyak for your valuable advice and comments while working on this article.

References

[1] K. Kholmurodov, K. Rahmonov, K. Qurboniyon, T. Zelenyak, A. Doroschkevich, P. Gladishev, T. Yamamoto, Open J. Phys.Chem. 5, 110-121 (2015); [2] T.Oku, Solar Cells - New Appr. and Rev. 2, 78-101, (2015); https://doi.org/10.5772/59284 [3] Y. Wang, Z. Yubo, Z. Peihong, Z. Wenqing, Phys. Chem. Chem. Phys. 17, 11516-11520, (2015); https://doi.org/10.1039/C5CP00448A [4] K. Chu, Y. Zhou, J-L. Song, C. Zhang, Polyhedron. 4, 1-21, (2017); https://doi.org/10.1016/j.poly.2017.04.015 [5] L. Gillon, G.R. Lewis, A.G. Orpen, S. Rotter, J. Starbuck, X-M. Wang, R.Y. Martin, C. Ruiz-Perez, J. Chem. Soc. 3897-3905, (2000); https://doi.org/10.1039/B0050361 [6] H. Mashiyama, Y. Kawamura, H. Kasano, T. Asahi, Y. Noda, H. Kimura, Ferroelectrics. 348, 182-186, (2007); https://doi.org/10.1080/00150190701196435 [7] E.P. Giannelis, J. of Adv. Mater. 8, 29-35, (1996); https://doi.org/10.1002/adma.19960080104 [8] K. Shreya, P. Padmini, K.N. Pabitra, J. of Physics D: Applied Phys. 54(13), (2020); https://doi.org/10.1088/1361-6463/abd0ad [9] J.P. González-Vázquez, V. Morales-Florez, J.A. Anta, J. Phys. Chem. Lett. 3, 386-393, (2012); https://doi.org/10.1021/jz2015988 [10] X. Guo, C. Burda, J. of Coord. Chem. Rev. 7, 1-16, (2016); https://doi.org/10.1016/j.ccr.2016.03.013 [11] D.Y. Liu, L. Kelly, J. of Nat. Phot. 8, 133–138, (2013); https://doi.org/10.1038/nphoton.2013.342

[12] Y. Zhao, K. Zhu, J. of Chem. Soc. Rev. 45, 655-689, (2016);

https://doi.org/10.1039/C4CS00458B

[13] K. Liang, D.B. Mitzi, M.T. Prikas, J. of Chem. Mater. 10, 403-411, (1998); https://doi.org/10.1021/cm970568f

[14] J. H. Im, H. S. Kim, N. G. Park, J. of APL Mat. 2, 081510, (2014); https://doi.org/10.1063/1.4891275

[15] J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. Van Schilfgaarde, J. of Nano Lett. 14, 2584–2590, (2014); <u>https://doi.org/10.1021/nl500390f</u>

[16] L. A. Frolova, D.V. Anokhin, A.A. Piryazev, P.A. Troshin, J. of Phys. Chem. Lett. 8, 67-72, (2016); <u>https://doi.org/10.1021/acs.jpclett.6b02594</u>

[17] J. W. Lee, D.H. Kim, H.S. Kim, S.W. Seo, S.M. Cho, N. G.Park, J. of Adv. Energy Mater. 5, 1-9, (2015); <u>https://doi.org/10.1002/aenm.201501310</u>

[18] F.Jafarzadeh, S.Javadpour, M. Shariat, J. of Ceram. Int. 43, 11552–11555, (2017); https://doi.org/10.1016/j.ceramint.2017.05.030

[19] T.Y. Zelenyak, K.T. Kholmurodov, A.R. Tameev, A.V. Vannikov, P.P. Gladyshev, J. of High Energy Chem. 50, 423- 428, (2016); <u>https://doi.org/10.1134/S0018143916050209</u>

[20] N. Chieng, X.Teo, M.H. Cheah, M.L. Choo, J. Chung, T.K. Hew, P.S. Keng, J. Pharm. Sci. 108, 3848-3858, (2019); <u>https://doi.org/10.1016/j.xphs.2019.09.013</u>

[21] T.M. Tiama, H. Elhaes, M.A. Ibrahim, J. of Letters in Applied NanoBioSci. 10, 2438-2445, (2021); <u>https://doi.org/10.33263/LIANBS103.24382445</u>

[22] H. Alıcı, K. Demir, J. of Chem. Phys. 542, 111057, (2021); https://doi.org/10.1016/j.chemphys.2020.111057

[23] H.A. Ezzat, I. Gomaa, A.E.D.A.Gawad, O. Osman, A.A. Mahmoud, M.S. Abdel-Aal, H. Elhaes, M.A. Ibrahim, J. of Letters in Applied NanoBioSci. 9, 1459 – 1466, (2020); https://doi.org/10.33263/LIANBS94.14591466

[24] R.Wang, J.Wang, Q. Song, J. of Construction and Building Materials. 268, 121081, (2021); https://doi.org/10.1016/j.conbuildmat.2020.121081

[25] E.H. Avdović, D.S. Dimić, M. Fronc, J. Kožišek, E. Klein, Z.B. Milanović, A. Kesić, Z.S. Marković, J. Mol. Struct. 1231, 129962, (2021); <u>https://doi.org/10.1016/j.molstruc.2021.129962</u>

[26] M. D. Graef, M. Mchenry, J.of. Cambridge University Press, 877, (2007);

[27] M.A. Pena, J. Fierro, J.of Chem. Rev. 101, 1981–2018, (2001);

https://doi.org/10.1021/cr980129f

[28] B. Cai, Y. Xing, Z. Yang, W-H. Zhang, J. Qiu, J.of Energy Environ. Sci. 6, 1480, (2013); https://doi.org/10.1039/C3EE40343B

[29] J. Haruyama, K. Sodeyama, L. Han, Y. Tateyama, J. Phys. Chem. Lett. 5, 2903–2909, (2014); https://doi.org/10.1021/jz501510v

[30] J.A. Souza, J.P. Rino, Acta Mater. 59, 1409-1423, (2011); https://doi.org/10.1016/j.actamat.2010.11.003.

[31] L. Taibi-Benziada, A. Mezroua, J.of Ceramics-Silikáty.48, 80-184, (2004);

[31] L. Taibi-Benziada, A. Mezroua, J.of Ceramics-Silikaty.48, 80-184, (2004); [22] M. Gullain M.T. David, E.K. Salin, J. Plana, Constants Matter 15, 2201, (200

[32] M. Calleja, M.T. Dove, E.K. Salje, J. Phys.: Condens. Matter. 15, 2301, (2003); http://stacks.iop.org/JPhysCM/15/2301

[33] B. Markus, K. Thorsten, W. Michael, J.of. Dalton Trans.46, 3500-3509, (2017); https://doi.org/10.1039/C6DT04796C

[34] T. Y. Zelenyak, K. R. Rakhmonov, K. T. Kholmurodov, P. P. Gladyshev, A. R. Tameev, High Energy Chem. 52, 433–439, (2018); https://doi.org/10.1134/S0018143918050168

[35] Y.Wang, Y. Zhang, P. Zhang, W. Zhang, J. of. Phys. Chem. Phys. 17, 11516-11520, (2015); https://doi.org/10.1039/C5CP00448A

[36] K. Cai, Y. Yang, J. Shi, Z. Zhong, Q. H. Qin, Appl. Surf. Sci. 149955,(2021); https://doi.org/10.1016/j.apsusc.2021.149955

[37] L.Y. Xu, Y. Alrefaei, Y.S. Wang, J.G. Dai, Constr. and Build. Mat. 276, 122196, (2021); https://doi.org/10.1016/j.conbuildmat.2020.122196

[38] H. Akbarzadeh, E. Mehrjouei, A.N. Shamkhali, S. Ramezanzadeh, M. Abbaspour, S. Salemi, Colloids Surf, A Physicochem Eng. Asp. 610, 125920, (2021); https://doi.org/10.1016/j.colsurfa.2020.125920

- [39] P. Paligaspe, S. Weerasinghe, D.P. Dissanayake, R. Senthilnithy, J. Mol. Struct.1235, 130257, (2021); <u>https://doi.org/10.1016/j.molstruc.2021.130257</u>
 [40] M. Khusenov, E. Dushanov, K. Kholmurodov, J. Modern Phys. 5, 137-144, (2014); <u>https://doi.org/10.4236/jmp.2014.54023</u>
- [41] J. Li, L. Jiang, X. Cao, Y. Wu, F. Lu, F. Liu, Y. Li, Y. Liu, Enzy. Microb. Tech. 147, 109787, (2021); https://doi.org/10.1016/j.enzmictec.2021.109787
- [42] J. Zemann, J. of Crys. Str. 18(1), 139, (1965); https://doi.org/10.1107/S0365110X65000361

33