

Atomistic Simulation of La and Mn-Doped $\text{PbBi}_2\text{Nb}_2\text{O}_9$ Aurivillius PhaseAkram La Kilo^{1,2*}, Ramona Nintias R. Abas¹, Alberto Costanzo³, Daniele Mazza³,
Deasy N. Botutihe^{1,2}, Jafar La Kilo^{1,2}¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bone Bolango Gorontalo, 96554, Indonesia²Department of Educational Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bonebolango Gorontalo, 96554, Indonesia³Dipartimento di Scienza dei Materiali e' Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

*Corresponding author email: akram@ung.ac.id

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ABSTRACT. This study aims to determine the effect of Mn^{3+} and La^{3+} dopants on the structure of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (PBN) using atomistic simulation. PBN phase geometry was optimized before the Mn^{3+} and La^{3+} doped phase. Mn^{3+} partially substituted octahedral Nb^{5+} in the perovskite layer. While La^{3+} partially substituted Bi^{3+} in the bismuth layer and dodecahedral Pb^{2+} in the perovskite layer. The concentration (x) of dopants that doped PBN was made in such a way that it produces a phase of $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, \text{ and } 0.3$) which was not charged. The simulation results showed that the optimized PBN cell parameters were in a good agreement with the experimental result. Increasing the concentration of dopants result in the $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ phase (PBNM-Bi and PBNM-A) being less stable, as indicated by the increased lattice energy. PBNLM-Bi structures experiences an elongation which was showed by the cell parameters of c increase while a and b decrease. La^{3+} prefers to occupy bismuth oxide layer rather than the dodecahedral A-site of the perovskite layer. The results of this simulation can explain the PBLNM structure of experimental results that do not pay attention to the multiplicity of doped PBN with certain dopant concentrations.

Keywords: Atomistic simulation, Aurivillius, lanthanide dopants, manganese and $\text{PbBi}_2\text{Nb}_2\text{O}_9$ **INTRODUCTION**

Aurivillius is a layered bismuth oxide that has potential applications in ferroelectric random access memory, a catalyst in the petrochemical industry, and is used as a sensor (Prakash et al., 2007). This oxide also plays a role in fuel cells, especially as an electrolyte because of its high ionic conductivity. Solid electrolyte materials with high oxide conductivity at low temperatures are intensively investigated to obtain solid oxide fuel cell that is capable of operating at low temperatures (Kilo et al., 2011). Because of the potential application, the oxide is widely studied and synthesized.

Aurivillius is a metal oxide compound consisting of a bismuth and perovskite layers with the general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ (Aurivillius, 1949a, 1949b). Cation A is an ion with a charge of +1, +2, and 3 which has dodecahedral coordination. Cation A is in the form of alkali metal, earth alkaline, rare-earth elements, or mixtures thereof. Cation B which is smaller than cation A is a transition element that has octahedral coordination. The number of octahedral in the perovskite layer is shown by integer's n with a value

of $1 \leq n \leq 8$. The electrical properties of Aurivillius can be improved by doping both the perovskite and the bismuth oxide layers. In the perovskite layer, the ions that can be substituted are in the A octahedral and dodecahedral sites. Meanwhile, Bi^{3+} substitution can only be done partially by certain metal ions so that the research results are still limited (Sadapu, 2015).

Aurivillius compound that attracts attention is $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (PBN) because it has ferroelectric properties. $\text{PbBi}_2\text{Nb}_2\text{O}_9$ has orthorhombic symmetry, $A2_1am$ group space with $a = b = 5,496$, and $c = 25.55 \text{ \AA}$, where Pb^{2+} occupies A site and Nb^{5+} occupies B site. In the two-layer Aurivillius of PBN there is found a cation disorder between Pb^{2+} and Bi^{2+} in the perovskite layer at high level. That is because Pb^{2+} and Bi^{2+} both have lone pairs and this cation has the same tendency to occupy the perovskite and bismuth layers. Cationic disorder can affect the Aurivillius structure that is produced because the sizes of Pb^{2+} and Bi^{2+} are different (Ismunandar et al., 1996). The result is a small distortion in this PBN as a determinant of ferroelectric properties.

In addition to ferroelectric properties, PBN can be ferroelectromagnetic by doping it with dopants that have free electrons in d orbital. Wendari *et al.* has successfully synthesized the Aurivillius $\text{PbBi}_2\text{Nb}_2\text{O}_9$ compound by partial substitution of La^{3+} for Bi^{3+} and Mn^{3+} for Nb^{5+} (Wendari *et al.*, 2019). In their study, non-polar single-phase samples were produced, with orthorhombic $A2_1am$ structures for $x = 0, 0.1, \text{ and } 0.3$. However, they did not confirm that the compounds produced were charged or not because they claimed that Pb^{2+} occupied partially Bi^{3+} site in the bismuth oxide layer. Besides, they also do not take into account the multiplicity of ions so that they cannot determine the possible site of dopants in compounds formed with variations of concentration ($x = 0.0, 0.1, \text{ and } 0.3$). Therefore, this research look for completion to explain these two things by means of atomistic simulation of $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0.0, 0.1, \text{ and } 0.3$) using the General Utility Lattice Program (GULP) code. The code uses the basis of classical atomistic simulation theory to study the various systems and properties of materials such as solid materials (Dutra *et al.*, 2021). Aurivillius is a solid material with a layered structure and has metal ions with large atomic numbers and many so that the code that can be used is GULP as reported by researchers (Islam *et al.*, 1998; Mczka *et al.*, 2011; Phillpot *et al.*, 2007; Snedden *et al.*, 2004; Xiaojing *et al.*, 2016; Yang *et al.*, 2018).

EXPERIMENTAL SECTION

Materials and Method

The device used in this simulation consists of hardware and software. The hardware used is a computer processor Intel (R) Core (TM) i5-8250U CPU @ 1.60GHz 1.80 GHz and RAM 4.00 GB. The software used is 64-bit Operating System, x64-based processor, Microsoft Windows 10 Pro 32-Bit and General Utility Lattice Program (GULP) code for atomistic simulation (Gale, 1997; Gale & Rohl, 2003).

The parent compound that was simulated was $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (PBN) from the results of X-ray diffraction and its neutrons reported by Miura (2002). Then, the optimized parent compound was doped with La^{3+} and Mn^{3+} ions with a certain concentration (x) to obtain $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0.0, 0.1, \text{ and } 0.3$) compounds. All compounds are made in an uncharged state, where the interactions between cations and anions are ionic interactions. As a result of this interaction, the interatomic potential used is the Buckingham potential. All these compounds were optimized at constant pressure with the conditions of the Newton-Raphson optimizer and BFGS hessian update, and the results were declared convergent if the Gnormal value was less than 0.01.

The simulation method uses atomistic with an energy minimization system that is carried out using GULP code. The basis of this simulation is the

interaction between ions in the crystal structure (Born & Mayer, 1932). Modeling interactions between ions can be understood through the function of potential energy to the system, especially the two-body system that describes these interactions. In the ion model, the short-range interaction is dominated mainly by the effect of the nearest neighbor ion. The short-range potential function can be described by Buckingham potential in the form of equation (1):

$$\theta_{ij} = A_{ij} \exp\left(\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where A_{ij} , ρ_{ij} , and C_{ij} are constants and r_i is the distance between ions. The first term in this equation represents a short-range repulsion, while the second term shows the pull of induced dipoles (van der Waals). In addition to the inter ion interaction, the model can also include ion polarization. The model describes the ion as a shell (depicting the outer valence electron cloud) bound to a large mass nucleus by a harmonious spring. Additional energy between the nucleus and the shell is expressed by equation (2):

$$U_3 = \sum_i k_i^s r_i^2 \quad (1)$$

Where k_i^s is the spring constant and r_i is the distance between the nucleus and shell. Equation (2) describes the ion polarization needed for the calculation of energy defects and dielectric constants. Ion polarization is formulated by equation (3):

$$\alpha_i = \sum \frac{(Y_i e)^2}{k_i^s} \quad (2)$$

where Y_i ada e are the shell charge and electron charge, respectively

In addition to the lattice energy generated from the atomistic simulation, structural stability of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ can be predicted by calculating the Goldschmidt perovskite tolerance formulated:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (4)$$

where r_A , r_B , and r_O are the ionic radii of cations A , B , and oxygen anions, respectively (Goldschmidt, 1926)

RESULTS AND DISCUSSION

$\text{PbBi}_2\text{Nb}_2\text{O}_9$ is a two-layer Aurivillius consisting of $(\text{Bi}_2\text{O}_2)^{2+}$ dan $(\text{Pb}_{n-1}\text{Nb}_n\text{O}_{3n+1})^{2-}$ layers, where n (the number of octahedral layers in the perovskite layer) is 2. All Bi^{3+} occupy the bismuth oxide layer while Pb^{2+} and Nb^{5+} occupy the perovskite layer respectively as A dodecahedral and B octahedral. These orthorhombic compounds have a space group $A2_1am$, where Bi^{3+} and Nb^{5+} have a multiplicity of 8, while the multiplicity of Pb^{2+} is 4. Oxygen in this structure occupies five sites each distinguished with O1, O2, O3, O4, and O5 with multiplicity 8, except O1 which has a multiplicity of 1.

Wendari *et al.* (2019) reported that the perovskite tolerance value calculated from $\text{PbBi}_2\text{Nb}_2\text{O}_9$ is 0.945 when the ionic radius of Pb^{2+} as a cation A is 1.29 Å (Shannon, 1976). This ionic radius is 8 coordination,

whereas the Pb^{2+} in perovskite is 12 coordination, with a radius of 1.49 Å, so the tolerance value for perovskite is 0.999. However, the difference between the two results is still categorized as a perovskite structure with a t value between 0.825 and 1.059. If $t = 1$, the structure formed by perovskite is an ideal cubic, while t which has a very large deviation from one is predicted to be an unstable structure.

The oxide is neutral; there are no vacancy and electrons that move freely. Therefore, although the calculation of the number of moles or the concentration of reagent material to form $\text{PbBi}_2\text{Nb}_2\text{O}_9$ compounds is correct, in the synthesis of compounds, it can produce electrons or vacancies. Synthesis results are difficult to obtain uncharged compounds, so

computational calculations are needed to overcome this. This simulation of this compound is uncharged with all its elements having occupancy of one. The results of the optimization of the geometry of these compounds are in good agreement with the experimental results as shown by the lattice parameters in **Table 1**. The difference between the parameter results of the simulation and the synthesis is small, namely 0.68, 1.81, and 0.53% for parameters of a , b , and c , respectively. This difference is a good agreement to the two layer Aurivillius of $\text{Bi}_3\text{TiNbO}_9$ reported by Rosyidah et al. (2008). For simple compounds that are not layered structures, they can have much smaller lattice parameter differences (La Kilo et al., 2019).

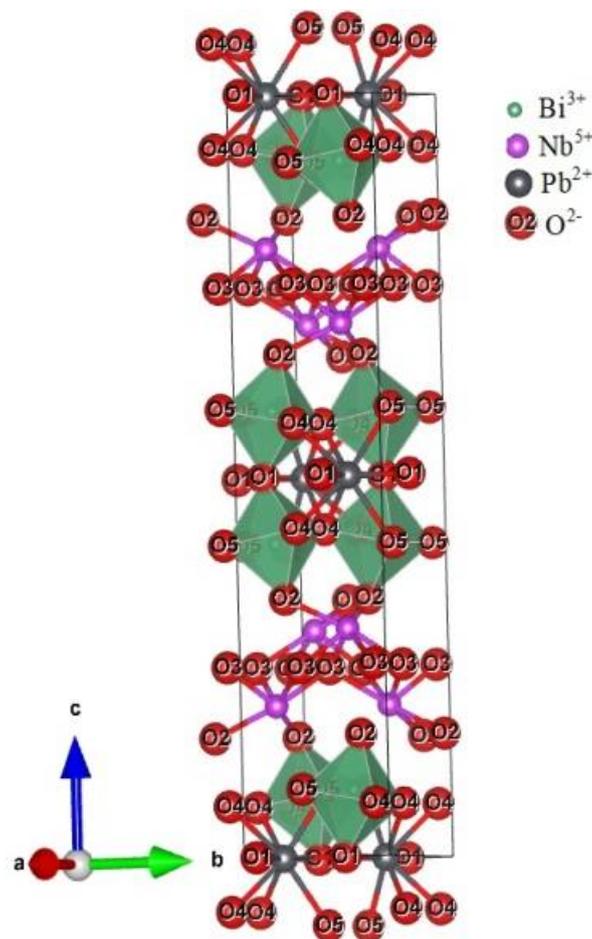


Figure 1. Crystal Structure of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (Wendari et al., 2019)

Table 1. Parameter cell of calculated and experimental $\text{PbBi}_2\text{Nb}_2\text{O}_9$

Parameter	Calculated	Exp.(Miura, 2002)	$\Delta_{(\text{exp-calc})}$ (%)
c (Å)	5.4587	5.4960	0.68
b (Å)	5.3965	5.4960	1.81
a (Å)	25.4154	25.550	0.53
$\alpha = \beta = \gamma$ (degree)	90	90	
Lattice energy (eV)	-1005.8448		

The a and b lattice parameters produced in this simulation are not the same as those reported by Miura *et al.*, but its are consistent with the results of the $\text{PbBi}_2\text{Nb}_2\text{O}_9$ synthesis reported by Kim *et al.* (2004). Cell parameters of a , b , and c are 5.503(4), 5.495(4), and 25.531(5), respectively. Aurivillius cell parameters with very small differences between experimental and simulation results have also been reported by several researchers. The difference in cell parameters is caused by differences in synthesis methods. The very small difference in cell parameters between the experimental and simulation results indicated that the simulated compound is correct and can be used as a standard of input data for simulating $\text{PbBi}_2\text{Nb}_2\text{O}_9$ doping with La^{3+} and Mn^{3+} .

In this study, La^{3+} dopant can occupy Bi^{3+} of $(\text{Bi}_2\text{O}_2)^{2+}$ or both bismuth oxide and A sites, while Mn^{3+} occupies B site. The five doping compounds produced in this study are denoted by PBNL, PBNLM-Bi-0.1, PBNLM-Bi-0.3, PBNLM-A-0.1, and PBNLM-A-0.3. PBNL is a compound of $\text{PbBi}_{1.5}\text{La}_{0.5}\text{Nb}_2\text{O}_9$ ($x = 0.0$) where all La^{3+} occupies a layer of $(\text{Bi}_2\text{O}_2)^{2+}$ with an occupancy of 25% of 1 Bi occupancy. PBNLM-Bi-0.1 is $\text{Pb}_{0.8}\text{Bi}_{1.7}\text{La}_{0.5}\text{Nb}_{1.9}\text{Mn}_{0.1}\text{O}_9$, where $x = 0.1$, La^{3+} occupies 0.25% of Bi site in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer, 5% of Mn^{3+} occupies the Nb^{5+} site in the octahedral layer of perovskite, and 20% of Bi^{3+} occupy the dodecahedral Pb^{2+} in the perovskite layer. PBNLM-Bi-0.3 is $\text{Pb}_{0.4}\text{Bi}_{2.1}\text{La}_{0.5}\text{Nb}_{1.7}\text{Mn}_{0.3}\text{O}_9$ ($x = 0.3$) where La^{3+} occupies 0.25% of the site of Bi^{3+} in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer, 15% of Mn^{3+} occupies the site of Nb^{5+} in the octahedral layer of perovskite, 60% of Bi^{3+} occupy the Pb^{2+} dodecahedral in the perovskite layer. PBNLM-A-0.1 is $\text{Pb}_{0.8}\text{La}_{0.7}\text{Bi}_{1.5}\text{Nb}_{1.9}\text{Mn}_{0.1}\text{O}_9$ ($x = 0.1$), where La^{3+} occupies 25% of the Bi^{3+} site in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer and 20% in Pb^{2+} ; Mn 5% occupies the site of Nb^{5+} in the perovskite octahedral layer. PBNLM-A-0.3 is $\text{Pb}_{0.4}\text{La}_{1.1}\text{Bi}_{1.5}\text{Nb}_{1.7}\text{Mn}_{0.3}\text{O}_9$, where $x = 0.3$, La^{3+} occupies 0.25% of the Bi^{3+} site in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer and 60% occupies the Pb^{2+} dodecahedral in the perovskite layer.

As a result of partial substitution to produce the five compounds, the stability of the structure is predicted from the average value of the ionic radius or bond length, which is formulated:

$$t = \frac{[(1-x)r_A + xr_{A'} + r_O]}{\sqrt{2}[(1-x)r_B + xr_{B'} + r_O]} \quad (5)$$

This tolerance involves partial substitution of cations A and/or B by A' and B', respectively, with a concentration of x . The results of the calculation of perovskite tolerance indicate that the presence of dopants in PBN causes the t value to decrease (Table 2) as an indication that the structures formed are increasingly orthorhombic. This reduction was more significant when La^{3+} occupied the perovskite layer rather than the bismuth layer due to the large ionic radii difference between La^{3+} (1.36 Å) and Pb^{2+} (1.49 Å) compared to the ionic radii of La^{3+} and Bi^{3+} (1.40 Å).

Simulation results of the compounds are shown in Figure 2. Lattice parameters of a , b , and c of the five Aurivillius compounds rise from their parent compounds. When $x = 0$, the cell parameter rises along with the radius of the La^{3+} (1.16 Å) which is greater than Bi^{3+} (1.17 Å) for 8-fold coordination (Shannon, 1976). The increase in parameters was even greater when La^{3+} was partially distributed in both layers of bismuth oxide and perovskite (PBNLM-A-0.1 and PBNLM-A-0.3). Conversely, when La^{3+} in the bismuth oxide layer and Bi^{3+} occupies A site in the perovskite layer, the cell parameters decrease. When compared with PBNL, the lattice parameter a tends to be constant, b decreases, and c increases for both PBNLM-Bi-0.1 and PBNLM-Bi-0.3 compounds. The cell parameter of the both compound is elongated. The increase in Bi occupancy in layer of A results in a larger octahedral distortion (Ismunandar *et al.*, 1996). Wendari reported that the cell parameter of a was relatively constant, while the lattice parameters of a and b decrease with increasing value of x . They propose that this is consistent with the ionic radius of Pb^{2+} which is greater than Bi^{3+} for 8-fold coordination, where Pb^{2+} is found in the Bi^{3+} layer. If so then we predict that the compound they have synthesized is not the neutral compounds of $\text{Pb}_{0.8}\text{Bi}_{1.7}\text{La}_{0.5}\text{Nb}_{1.9}\text{Mn}_{0.1}\text{O}_9$ and $\text{Pb}_{0.4}\text{Bi}_{2.1}\text{La}_{0.5}\text{Nb}_{1.7}\text{Mn}_{0.3}\text{O}_9$ as they claim (Wendari *et al.*, 2019).

Table 2. Perovskite tolerance factor of La^{3+} and Mn^{3+} -doped $\text{PbBi}_2\text{Nb}_2\text{O}_9$ aurivillius phase

Dopant composition (x)	Aurivillius	t	t (Wendari <i>et al.</i> , 2019)
0.0	PBNL	0.999	0.945
0.1	PBNLM-Bi-0.1	0.993	0.944
	PBNLM-A-0.1	0.990	
0.3	PBNLM-Bi-0.3	0.980	0.940
	PBNLM-A-0.3	0.972	

The t value of this calculation is different from $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ that reported (Wendari *et al.*, 2019) because in addition to the difference in the value of the Pb^{2+} ionic radius, it is also the distribution of the dopant composition at position A in the perovskite layer and the position of Bi in $(\text{Bi}_2\text{O}_2)^{2+}$.

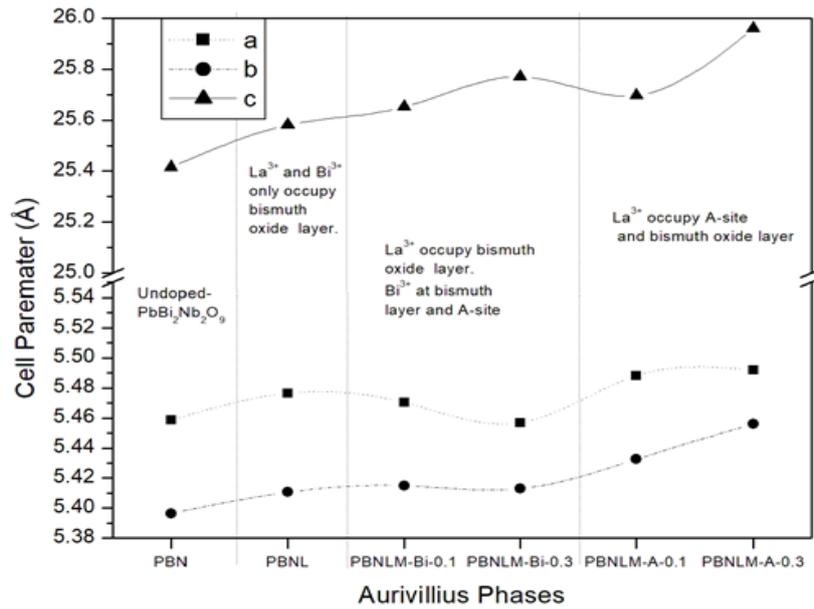


Figure 2. Lattice parameter of La^{3+} and Mn^{3+} -doped $\text{PbBi}_2\text{Nb}_2\text{O}_9$ Aurivillius Phase

Table 3. Interatomic potential of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$

	A (eV)	ρ (Å)	C (eV Å)
a) Buckingham short range			
Pb...O	5564.374	0.2610	0.0
Nb...O	1796.30	0.3459	0.0
Bi...O	49529.35	0.2223	0.0
O...O	9547.96	0.2192	32.0
b) Shell model			
Species	k (eVÅ ²)	Shell (e)	
Pb ²⁺	205.00	1.00	
Nb ⁵⁺	1358.58	-4.497	
Bi ³⁺	359.55	-5.51	
O ²⁻	6.3	-2.04	

The lattice parameter is also affected by the polarization of ions. In this study, the polarization strength of cations is $\text{Bi}^{3+} > \text{Nb}^{5+} > \text{Pb}^{2+}$. While the polarization of the Mn^{3+} and La^{3+} ions is zero because all charges are centered on the core (+3). Due to ion polarization, the bismuth oxide layer and perovskite layer is distorted as reinforced by the report of Shikawa *et al.* in $\text{SrBi}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_9$ compounds (Shimakawa *et al.*, 2000). Such distortion also indicates that an ion in a compound no longer has a perfect Bond Valence Sum (BVS) (Kilo *et al.*, 2011; La Kilo & Mazza, 2011). The ion polarization in this study was modeled with a shell model as shown in **Table 3**.

Based on **Table 3**, the repulsive force between cationic and anionic shells is $\text{Bi}\dots\text{O} > \text{Pb}\dots\text{O} > \text{Nb}\dots\text{O}$ as shown in the Buckingham potential. This indicated that the number of Bi^{3+} ions which replace A ion in perovskite layer is only partially compared to Pb^{2+} ion. However, the two ions have the same chemical character, namely the presence of lone pair electron in s^2 orbital (La Kilo *et al.*, 2020). The electron pair in

bismuth oxide layer causes elongation in the PBNLM-Bi-0.1 and PBNLM-Bi-0.3 structures. This is consistent with the report of Sadapu *et al.* that the increase in c cell parameter is due to the repulsion effect of the free electron pair of Bi^{3+} in the bismuth oxide layer of $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ba}, \text{Ca}, \text{Sr}, \text{and Pb}$) (Sadapu, 2015). The increase in ionic polarization as a result of the increase of displacement along the axes of a and b (Shimakawa *et al.*, 2000).

$\text{PbBi}_2\text{Nb}_2\text{O}_9$ lattice energy is much smaller than the $\text{Bi}_3\text{TiNbO}_9$ lattice energy reported by Rosyidah *et al.* (Rosyidah *et al.*, 2008). The more the number of octahedral layers in the perovskite, the more negative the Aurivillius lattice energy of the compound. This compound is a two-layer Aurivillius which in theory will have more energy than the Aurivillius lattice energy with the octahedral layer above it. But these results are contrary to what is expected. In fact, $\text{PbBi}_2\text{Nb}_2\text{O}_9$ has a lower lattice energy compared to the four-layer Aurivillius lattice energy of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (-770.64590 eV) and $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ (-927.2781 eV), which means

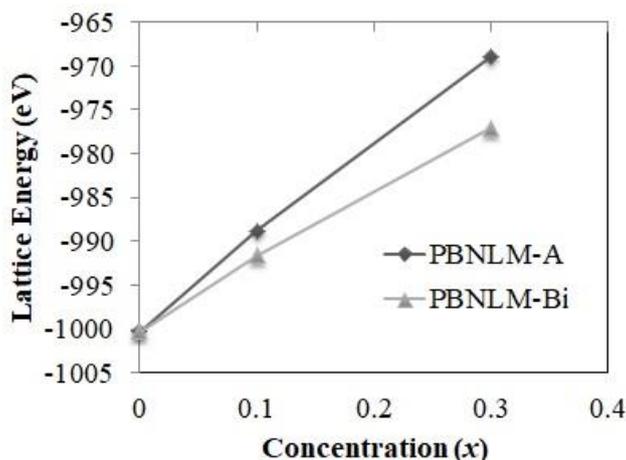


Figure 3. Lattice Energy of Mn^{3+} and La^{3+} -doped $\text{PbBi}_2\text{Nb}_2\text{O}_9$

that the $\text{PbBi}_2\text{Nb}_2\text{O}_9$ lattice energy is very stable so it is not surprising if many researchers try to modify this structure as a potential as ferro electromagnetic material in industry. When $\text{PbBi}_2\text{Nb}_2\text{O}_9$ is doped with La^{3+} and Mn^{3+} , the resulting Aurivillius lattice energy are becoming greater as shown in Figure 3.

PBNLM-Bi-0.1 and PBNLM-Bi-0.3 lattice energy is smaller than PBNLM-A-0.1 and PBNLM-A-0.3. That is, the Pb^{2+} substitution in the perovskite layer is easier to occur by Bi^{3+} than La^{3+} dopants. This also confirms that the elongation of $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ structure with an increase in concentration ($x = 0, 0.1,$ and 0.3) because Bi^{3+} which occupies the perovskite layer replaces the site of A (Pb^{2+}), not (Bi_2O_2) $^{2+}$ layer as shown reported by Wendari *et al.* (2019). This indicates that PBNLM-Bi is easier to synthesize than PBNLM-A. However, La^{3+} that enters both layers from Aurivillius, it is predicted that the structure of the compound will be more distorted, and in a higher concentration of La^{3+} dopant, Aurivillius compound will not be formed. Luckily, the Mn^{3+} that enters is only at site of B and in small amounts, partially substitutes Nb^{5+} which carries ferroelectric properties. Mn^{3+} which has four unpaired electrons in the d orbital causes Aurivillius to also have magnetic properties. These no spherical d orbital add to the octahedral distortion of the perovskite layer.

CONCLUSIONS

The atomistic simulation results were in good agreement with the experimental results based on the lattice parameters of the parent compound, $\text{PbBi}_2\text{Nb}_2\text{O}_9$. Bi^{3+} which partially substituted Pb^{2+} in the perovskite layer causes the structure of $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1,$ and 0.3) to elongate. Conversely, if Pb^{2+} was substituted by La^{3+} then that elongation did not occur. La^{3+} prefers to occupy bismuth oxide layer rather than the dodecahedral A-site of the perovskite layer. Increasing the concentration of dopants results Mn^{3+} and La^{3+} -doped $\text{PbBi}_2\text{Nb}_2\text{O}_9$ phase being less stable. PBNLM-Bi is

predicted more easily synthesized compared to PBNLM-A.

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