MOLEKUL
Print ISSN: 1907-9761 e-ISSN:2503-0310

HOME ABOUT USER HOME SEARCH CURRENT ARCHIVES

Home > User > Author > Submissions > #725 > **Summary**

#725 Summary

SUMMARY REVIEW EDITING

Submission

Authors	Akram La Kilo, Ramona Nintias R. Abas, Alberto Costanzo, Daniele Mazza, Deasy N. Botutihe, Jafar La Kilo
Title	Atomistic Simulation of La and Mn-Doped PbBi2Nb2O9 Aurivillius Phase
Original file	725-2057-1-SM.DOCX 2020-11-09
Supp. files	None
Submitter	Dr Akram La Kilo ✉
Date submitted	November 9, 2020 - 03:16 AM
Section	Articles
Editor	Ely Setiawan ✉
Author comments	1. Dr. Rolan Rusli, M.Si., email: rolan@rolanrusli.com 2. Dr. Atiek Rostika Noviyanti, M.Si. email: atiek.noviyanti@unpad.ac.id

Status

Guide for Authors
View Articles
Submit your paper
Editorial Board
Focus and Scope
Publication Ethics
Peer Review Process
Plagiarism Policy

Status	Archived
Initiated	2022-07-22
Last modified	2022-07-22

Submission Metadata

EDIT METADATA

Authors

Name	Akram La Kilo
ORCID iD	http://orcid.org/0000-0002-4885-1838
URL	https://scholar.google.co.id/citations?user=YWz4wUMAAAAJ&hl=id
Affiliation	Universitas Negeri Gorontalo
Country	Indonesia
Bio Statement	—

Principal contact for editorial correspondence.

Name	Ramona Nintias R. Abas
Affiliation	Universitas Negeri Gorontalo
Country	Indonesia
Bio Statement	—
Name	Alberto Costanzo
Affiliation	Politecnico di Torino
Country	Italy
Bio Statement	—
Name	Daniele Mazza
Affiliation	Politecnico di Torino
Country	Italy
Bio Statement	—
Name	Deasy N. Botutihe
URL	https://scholar.google.co.id/citations?user=UiY3It8AAAAJ&hl=id&oi=sra
Affiliation	State University of Gorontalo
Country	Indonesia


Molekul

Q3 Chemistry (miscellaneous) best quartile

SJR 2021 0.26

powered by scimagojr.com

Indexing and Abstracting:

Scopus

INDEX COPERNICUS INTERNATIONAL

DOAJ DIRECTORY OF OPEN ACCESS JOURNALS

CAS A DIVISION OF THE AMERICAN CHEMICAL SOCIETY

Google scholar

Crossref

sinta Science and Technology Index

Bio Statement	—
Name	Jafar La Kilo
ORCID iD	http://orcid.org/0000-0002-6995-7359
URL	https://scholar.google.co.id/citations?user=TFQkxv4AAAAJ&hl=en
Affiliation	Universitas Negeri Gorontalo
Country	Indonesia
Bio Statement	—

Title and Abstract

Title: Atomistic Simulation of La and Mn-Doped PbBi2Nb2O9 Aurivillius Phase

Abstract:

This study aims to determine the effect of Mn^{3+} and La^{3+} dopants on the structure of $PbBi_2Nb_2O_9$ (PBN) using atomistic simulation. PBN phase geometry is optimized before the phase is doped with Mn^{3+} and La^{3+}. Mn^{3+} partially substitutes octahedral Nb^{5+} in the perovskite layer. While La^{3+} partially substitute Bi^{3+} in the bismuth layer and dodecahedral Pb^{2+} in the perovskite layer. The concentration (x) of dopants that doped PBN is made in such a way that it produces a phase of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ (x = 0, 0.1, and 0.3) which is not charged. The simulation results show that the optimized PBN cell parameters are in a good agreement with the experimental result. Increasing the concentration of dopants result in the $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ phase (PBNM-Bi and PBNM-A) being less stable, as indicated by the increased lattice energy. PBNLM-Bi structures experiences an elongation which is 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.

Indexing

Language: en

Detail Statistic

Visitors

ID	77,905	VN	312
US	4,440	TR	228
IN	1,548	IR	218
CN	952	KR	214
PH	942	DE	201
MY	715	TW	195
TH	571	GB	183
JP	494	NG	180
BR	435	PK	177
RU	318	SG	173

Pageviews: 265,564

FLAG counter

Dokumen Akreditasi

- Sertifikat Akreditasi 2015
- SK Akreditasi 2018
- SK Akreditasi 2020
- Sertifikat Akreditasi 2020

USER

You are logged in as...
akram

- My Journals
- My Profile
- Log Out

FONT SIZE

Supporting Agencies

Agencies —

Molekul

Jurnal Ilmiah Kimia
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Jenderal Soedirman, Purwokerto, Indonesia

MOLEKUL
Print ISSN: 1907-9761 e-ISSN:2503-0310

HOME ABOUT USER HOME SEARCH CURRENT ARCHIVES

Home > User > Author > Submissions > #725 > **Review**

#725 Review

SUMMARY **REVIEW** EDITING

Submission

Authors	Akram La Kilo, Ramona Nintias R. Abas, Alberto Costanzo, Daniele Mazza, Deasy N. Botutihe, Jafar La Kilo
Title	Atomistic Simulation of La and Mn-Doped $PbBi_2Nb_2O_9$ Aurivillius Phase
Section	Articles
Editor	Ely Setiawan

Peer Review

Round 1

Review Version	725-2058-1-RV.DOCX 2020-11-09
Initiated	—
Last modified	—
Uploaded file	None

Editor Decision

Guide for Authors
View Articles
Submit your paper
Editorial Board
Focus and Scope
Publication Ethics
Peer Review Process
Plagiarism Policy

Decision	Accept Submission 2022-03-15		
Notify Editor	Editor/Author Email Record 2022-02-06		
Editor Version	None		
Author Version	725-2223-1-ED.DOCX	2021-03-06	DELETE
	725-2223-2-ED.DOCX	2022-02-06	DELETE
Upload Author Version	Choose File No file chosen	Upload	

Molekul

Jurnal Ilmiah Kimia
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Jenderal Soedirman, Purwokerto, Indonesia

Indexing and Abstracting:

Detail Statistic

Visitors

ID	77,905	VN	312
US	4,440	TR	228
IN	1,548	IR	218
CN	952	KR	214
PH	942	DE	201
MY	715	TW	195
TH	571	GB	183
JP	494	NG	180
BR	435	PK	177
RU	318	SG	173

Pageviews: 265,564

Dokumen Akreditasi

- Sertifikat Akreditasi 2015
- SK Akreditasi 2018
- SK Akreditasi 2020
- Sertifikat Akreditasi 2020

USER

You are logged in as...
akram

- My Journals
- My Profile
- Log Out

FONT SIZE

Editor/Author Correspondence

Editor
2020-12-22
07:53 AM

Subject: [JM] Editor Decision DELETE

Dr Akram La Kilo:

We have reached a decision regarding your submission to Molekul, "Atomistic Simulation of La and Mn-Doped PbBi2Nb2O9 Aurivillius Phase".

Our decision is: Revisions Required

Please allow our guidelines (https://ojs.jmolekul.com/ojs/index.php/jm/about/submissions#authorGuidelines) :
1. Manuscript should in general about 3000-5000 words (12 printed pages) including figures and tables.
2. The reference style used according to the APA (American Psychological Association) 6th edition.
3. The references used should be a minimum of 80% up to date reference (maximum of 10 years).
4. Please be aware of self-citation.

Ely Setiawan
Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Universitas Jenderal Soedirman, Purwokerto
elsant_13@yahoo.com
Editor
MOLEKUL - Scientific Journal in Chemistry

Author
2021-03-06
01:24 PM

Subject: Atomistic Simulation of La and Mn-Doped PbBi2Nb2O9 Aurivillius Phase DELETE

Dear Ely Setiawan

Thank you for providing valuable corrections to our manuscript. We have refined this manuscript based on reviewers' in-depth reviews. Next, we await some good news in the process of our article.

Best regards,

Akram La Kilo
Editor
MOLEKUL - Scientific Journal in Chemistry

Editor 2021-08-18 02:14 PM

Subject: [JM] Editor Decision

DELETE

Dear authors,

We have reached a decision regarding your submission to Molekul, "Atomistic Simulation of La and Mn-Doped PbBi2Nb2O9 Aurivillius Phase". Please revise according to the suggestion.

Our decision is: Revisions Required

Reviewer #1 comments :
1. The lattice optimization with different dopant concentration was not time dependent. Why the terminology of “atomistic simulation” was chosen than “atomistic modelling”?
2. Author only use single primary reference (Wendari,2019) in explaining the structural properties of doped PBN. Here, author can enrich with the other references which has alike system.
3. the author was not clearly yet explaining the urgency and the novelty of the research
4. Author was not mention yet the rational of the use of the GULP than other method.
5. Which Interatomic potentials was use to modelling the interaction? And why use that?
6. The procedure of modelling and calculation properties should be detailed
7. The structural stability formula (t) should be in the method section not in the discussion section
8. If possible, the visualization of the optimized systems should be shown in discussion section
9. The author compared the results of t with a single reference only, the more references will provide a broad view to the reader and also strengthen the results

Reviewer #2 comments:
1. the title is too general for a publication. I suggest changing the title to a ‘sharper’ title.
2. the employed English still need to be improved. There are a lot of typos and some of the sentences are hard to be read.

3. if I am correct in this manuscript, the author only used Buckingham and shell model for the polarization. In this field, I believe that DFT still better than classical potential. Did the author compare their results, especially in the ion polarization with DFT based results ?
4. for the computational methodology, it is not clear for me ? What did the author want to say ? Geometry optimization ? Molecular simulation ? I suggest to re write this section
5. for the general users, the result and discussion part are difficult to understand because it lacks the structural figures. I suggest adding some figures to depict the crystal structures of the materials.
6. based on the table 3, the author stated that ‘the repulsive force between cationic and anionic shells is Bi...O>Pb...O>Nb...O’. why did the author conclude this ? I believe there is a typo in the Table 3 too.

Thank you.

Best regards,

Editor
Ely Setiawan
Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Universitas Jenderal Soedirman, Purwokerto
elsant_13@yahoo.com
Editor
MOLEKUL - Scientific Journal in Chemistry

Author
2022-02-06
10:54 AM

Subject: Atomistic Simulation of La and Mn-Doped PbBi2Nb2O9 Aurivillius Phase

DELETE

Dear Editor

Thanks to the reviewers who have corrected this manuscript properly. Thanks also to the editors who have given the opportunity to improve it.

Regarding the review from the reviewer, we have corrected it according to the results of the review. Of course, not all of us can fix it because considering the code for the simulation using the DFT method, we don't have to solve the case of Aurivillius material which is layered and has many electrons from several metal ions.

Regards,

ALK
Editor
MOLEKUL - Scientific Journal in Chemistry

Close

Atomistic Simulation of La and Mn-Doped $PbBi_2Nb_2O_9$ Aurivillius Phase

Akram La Kilo[1,2], Ramona Nintias R. Abas[1], Alberto Costanzo[3], Daniele Mazza[3], Deasy N. Botutihe[1,2], Jafar La Kilo [1,2]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, State University of Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bonebolango Gorontalo, 96554, Indonesia

[2]Department of Educational Chemistry, Faculty of Mathematics and Natural Sciences, State University of Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bonebolango Gorontalo, 96554, Indonesia

[3]Dipartimento di Scienza dei Materiali e' Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

Correspondence: E-mail: akram@ung.ac.id

Abstrak

This study aims to determine the effect of Mn^{3+} and La^{3+} dopants on the structure of $PbBi_2Nb_2O_9$ (PBN) using atomistic simulation. PBN phase geometry is optimized before the phase is doped with Mn^{3+} and La^{3+}. Mn^{3+} partially substitutes octahedral Nb^{5+} in the perovskite layer. While La^{3+} partially substitute Bi^{3+} in the bismuth layer and dodecahedral Pb^{2+} in the perovskite layer. The concentration (x) of dopants that doped PBN is made in such a way that it produces a phase of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ ($x = 0$, 0.1, and 0.3) which is not charged. The simulation results show that the optimized PBN cell parameters are in a good agreement with the experimental result. Increasing the concentration of dopants result in the $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ phase (PBNM-Bi and PBNM-A) being less stable, as indicated by the increased lattice energy. PBNLM-Bi structures experiences an elongation which is 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

Aurivillius; $PbBi_2Nb_2O_9$; Atomistic simulation; Manganese and lanthanide dopants

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 $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ (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 $PbBi_2Nb_2O_9$ (PBN) because it has ferroelectric properties. $PbBi_2Nb_2O_9$ has orthorhombic symmetry, *A21am* group space with $a = b = 5{,}496$, and $c = 25.55$ Å, 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 $PbBi_2Nb_2O_9$ 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 A21am structures for x = 0, 0.1, 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, and 0.3). Therefore, this research looks for look for completion to explain these two things by means of atomistic simulation of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ (x = 0.0, 0.1, and 0.3) using the General Utility Lattice Program code.

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).

Simulations performed on the parent compound, namely: $PbBi_2Nb_2O_9$ (PBN). 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):

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

Where A_{ij}, ρ_{ij}, and C_{ij} are constants and ri 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):

$$U_3 = \sum_i k_i^s\, r_i^2 \qquad (2)$$

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):

$$\alpha_i = \sum \frac{(Yi\ e)^2}{k_i^s} \qquad (3)$$

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

Results and Discussion

PbBi$_2$Nb$_2$O$_9$ is a two-layer Aurivillius consisting of $(Bi_2O_2)^{2+}$ dan $(Pb_{n-1}Nb_nO_{3n+1})^{2-}$ 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 as shown in **Figure 1**. These orthorhombic compounds have a space group *A21am*, 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.

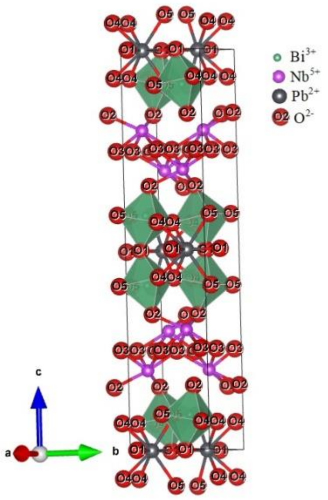


Figure 1. Crystal Structure of PbBi$_2$Nb$_2$O$_9$

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 PbBi$_2$Nb$_2$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 egreement to the two layer Aurivillius of Bi_3TiNbO_9 reported by Rosyidah *et al.* (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).

Table 1. Parameter Cell of Calculated and Experimental $PbBi_2Nb_2O_9$

Parameter	Calculated	Exp.(Miura, 2002)	$\Delta_{(exp-calc)}$ (%)
c (Å)	5.4587	5.4960	0.68
b (Å)	5.3965	5.4960	1.81
c (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 $PbBi_2Nb_2O_9$ synthesis reported by Kim *et al*. (Kim *et al.*, 2004). Cell parameters of *a, b,* and *c* are 5.503(4), 5.495(4), and 25.531(5), respectively. Aurivllius 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 $PbBi_2Nb_2O_9$ doping with La^{3+} and Mn^{3+}.

In this study, La^{3+} dopant can occupy Bi^{3+} of $(Bi_2O_2)^{2+}$ 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 $PbBi_{1.5}La_{0.5}Nb_2O_9$ (x = 0.0) where all La^{3+} occupies a layer of

$(Bi_2O_2)^{2+}$ with an occupancy of 25% of 1 Bi occupancy. PBNLM-Bi-0.1 is $Pb_{0.8}Bi_{1.7}La_{0.5}Nb_{1.9}Mn_{0.1}O_9$, where $x = 0.1$, La^{3+} occupies 0.25% of Bi site in the $(Bi_2O_2)^{2+}$ 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 $Pb_{0.4}Bi_{2.1}La_{0.5}Nb_{1.7}Mn_{0.3}O_9$ ($x = 0.3$) where La^{3+} occupies 0.25% of the site of Bi^{3+} in the $(Bi_2O_2)^{2+}$ 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 $Pb_{0.8}La_{0.7}Bi_{1.5}Nb_{1.9}Mn_{0.1}O_9$ ($x = 0.1$), where La^{3+} occupies 25% of the Bi^{3+} site in the $(Bi_2O_2)^{2+}$ layer and 20% in Pb^{2+}; Mn 5% occupies the site of Nb^{5+} in the perovskite octahedral layer. PBNLM-A-0.3 is $Pb_{0.4}La_{1.1}Bi_{1.5}Nb_{1.7}Mn_{0.3}O_9$, where $x = 0.3$, La^{3+} occupies 0.25% of the Bi^{3+} site in the $(Bi_2O_2)^{2+}$layer and 60% occupies the Pb^{2+} dodecahedral in the perovskite layer. Simulation results of the compounds are shown in **Figure 2.**

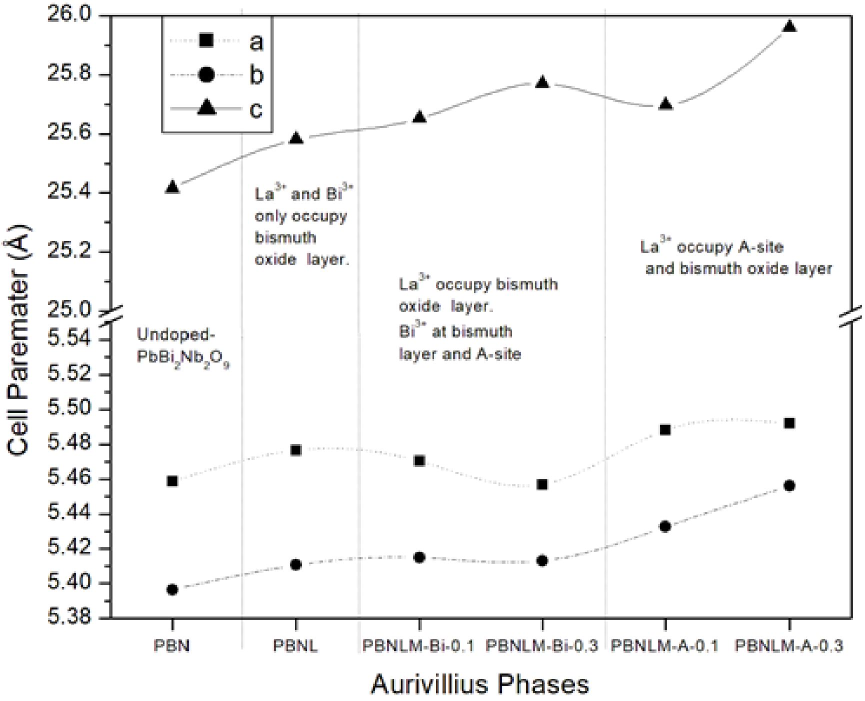


Figure 2. Lattice parameter of La^{3+} and Mn^{3+}-doped $PbBi_2Nb_2O_9$ Aurivillius Phase

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. 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 not the neutral compounds of $Pb_{0.8}Bi_{1.7}La_{0.5}Nb_{1.9}Mn_{0.1}O_9$ and $Pb_{0.4}Bi_{2.1}La_{0.5}Nb_{1.7}Mn_{0.3}O_9$ as they claim (Wendari et al., 2019).

The lattice parameter is also affected by the polarization of ions. In this study, the polarization strength of cations is $Bi^{3+}>Nb^{5+}>Pb^{2+}$. 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 $SrBi_2(Ta_{1-x}Nb_x)_2O_9$ 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 1.**

Table 2. Interatomic potential of $PbBi_2Nb_2O_9$ and $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$

	A (eV)	*ρ* (Å)	*C* (eV Å)
a) Buckingham short range			
b...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	

Based on **Table 2**, the repulsive force between cationic and anionic shells is Bi...O>Pb...O>Nb...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 bisumth 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 $ABi_4Ti_4O_{15}$ (A = Ba, Ca, Sr, and Pb) (Sadapu, 2015).

$PbBi_2Nb_2O_9$ lattice energy is much smaller than the Bi_3TiNbO_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 Aurivillus which in theory will have more energy than the Aurivilius lattice energy with the octahedral layer above it. But these results are contrary to what is expected. In fact, $PbBi_2Nb_2O_9$ has a lower lattice energy compared to the four layer Aurivillius lattice energy of $BaBi_4Ti_4O_{15}$ (-770.64590 eV) and $Ba_2Bi_4Ti_5O_{18}$ (-927.2781 eV), which means that the $PbBi_2Nb_2O_9$ lattice energy is very stable so it is not surprising if many researchers try to modify this structure as a potential as ferroelectromagnetic material in industry. When $PbBi_2Nb_2O_9$ is doped with La^{3+} and Mn^{3+}, the resulting Aurivillius lattice energy are becomes greater as shown in **Figure 3**.

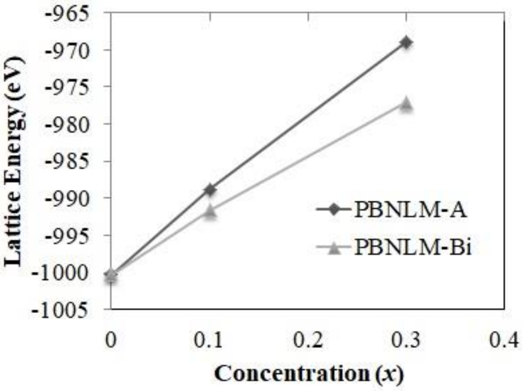


Figure 3. Lattice Energy of Mn^{3+} and La^{3+}-doped $PbBi_2Nb_2O_9$

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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ 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 (Pb2 +), not $(Bi_2O_2)^{2+}$ layer as shown reported by Wendari *et al.* (2019).

Conclusion

The atomistic simulation results are in good agreement with the experimental results based on the lattice parameters of the parent compound, $PbBi_2Nb_2O_9$. Bi^{3+} which partially substitutes Pb2 + in the perovskite layer causes the structure of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ (x = 0, 0.1, and 0.3) to elongate. Conversely, if Pb^{2+} is substituted by La^{3+} then that elongation does 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 $PbBi_2Nb_2O_9$ phase being less stable. PBNLM-Bi is more easily synthesized compared to PBNLM-A.

References

Aurivillius, B. (1949a). Mixed Bismuth Oxides with Layer lattices: I The Structure Type of CaBi2Nb2O9. *Arkiv Kemi Band I*.

Aurivillius, B. (1949b). Mixed bismuth oxides with layer lattices. II. Structure of Bi4Ti3O12. *Arkiv for Kemi*.

Born, M., & Mayer, J. E. (1932). Zur Gittertheorie der Ionenkristalle. *Zeitschrift Für Physik*. https://doi.org/10.1007/BF01340511

Gale, J. D. (1997). GULP: A computer program for the symmetry-adapted simulation of solids. *Journal of the Chemical Society - Faraday Transactions*. https://doi.org/10.1039/a606455h

Gale, J. D., & Rohl, A. L. (2003). The General Utility Lattice Program (GULP). *Molecular Simulation*. https://doi.org/10.1080/0892702031000104887

Ismunandar, Kennedy, B. J., Gunawan, & Marsongkohadi. (1996). Structure of ABi2Nb2O9 (A = Sr, Ba): Refinement of powder neutron diffraction data. *Journal of Solid State Chemistry*. https://doi.org/10.1006/jssc.1996.0321

Kilo, A. La, Prijamboedi, B., Martoprawiro, M. A., & Ismunandar. (2011). Modeling ionic conduction in γ-Bi 2VO 5.5. *Proceedings - International Conference on Instrumentation, Communication, Information Technology and Biomedical Engineering 2011, ICICI-BME 2011*. https://doi.org/10.1109/ICICI-BME.2011.6108652

Kim, H. G., Hwang, D. W., & Lee, J. S. (2004). An undoped, single-phase oxide photocatalyst working under visible light. *Journal of the American Chemical Society*. https://doi.org/10.1021/ja049676a

La Kilo, A., Costanzo, A., Mazza, D., Martoprawiro, M. A., Prijamboedi, B., & Ismunandar. (2020). Highest ionic conductivity of BIMEVOX (Me = 10% cu, 10% ga, 20% ta): Computational modeling and simulation. *Indonesian Journal of Chemistry*. https://doi.org/10.22146/ijc.42635

La Kilo, A., & Mazza, D. (2011). Pemodelan Konduktivitas Ion Dalam Struktur Li2sc3 (po4) 3 (Modeling Ionic Conductivity in Li2sc3 (po4) 3 Structure). *Jurnal Manusia Dan Lingkungan*, *18*(3), 179–183.

La Kilo, A., Umamah, T. S., & Laliyo, L. A. R. (2019). Study on the Stability of Trivalent Cations Doped Zirconia through Atomistic Modeling. *Jurnal Kimia Sains Dan Aplikasi*. https://doi.org/10.14710/jksa.22.4.129-135

Miura, K. (2002). Electronic properties of ferroelectric SrBi2Ta2O 9, SrBi2Nb2O9, and PbBi 2Nb2O9 with optimized structures. *Applied Physics Letters*. https://doi.org/10.1063/1.1474607

Prakash, P., Garg, A., Roy, M. K., & Verma, H. C. (2007). Novel low-temperature synthesis of ferroelectric neodymium-doped bismuth titanate nanoparticles. *Journal of the American Ceramic Society*. https://doi.org/10.1111/j.1551-2916.2007.01539.x

Rosyidah, A., Onggo, D., Khairurrijal, & Ismunandar. (2008). Atomic simulations of Aurivillius oxides: Bi3TiNbO9, Bi4Ti3O12, BaBi4Ti4O 15 and Ba2Bi4Ti5O18 doped with Pb, Al, Ga, In, Ta. *Journal of the Chinese Chemical Society*. https://doi.org/10.1002/jccs.200800018

Sadapu, S. (2015). Pengaruh Subtitusi Bi secara Parsial oleh Dopan (A= Ba, Ca, Sr dan Pb) dalam Lapisan [Bi2O2] 2+ pada Oksida Aurivillius ABi4Ti4O15. *Skripsi*, *1*(441410014).

Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*. https://doi.org/10.1107/S0567739476001551

Shimakawa, Y., Kubo, Y., Tauchi, Y., Kamiyama, T., Asano, H., & Izumi, F. (2000). Structural distortion and ferroelectric properties of SrBi2(Ta1-xNbx)2O9. *Applied Physics Letters*. https://doi.org/10.1063/1.1319509

Wendari, T. P., Arief, S., Mufti, N., Suendo, V., Prasetyo, A., Ismunandar, Baas, J., Blake, G. R., & Zulhadjri. (2019). Synthesis, structural analysis and dielectric properties of the double-layer Aurivillius compound Pb1-2xBi1.5+2xLa0.5Nb2-xMnxO9. *Ceramics International*, *45*(44), 17276–17282. https://doi.org/10.1016/j.ceramint.2019.05.285

Atomistic Simulation of La and Mn-Doped $PbBi_2Nb_2O_9$ Aurivillius Phase

Akram La Kilo[1,2], Ramona Nintias R. Abas[1], Alberto Costanzo[3], Daniele Mazza[3], Deasy N. Botutihe[1,2], Jafar La Kilo [1,2]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, State University of Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bonebolango Gorontalo, 96554, Indonesia

[2]Department of Educational Chemistry, Faculty of Mathematics and Natural Sciences, State University of Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bonebolango Gorontalo, 96554, Indonesia

[3]Dipartimento di Scienza dei Materiali e' Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

Correspondence: E-mail: akram@ung.ac.id

Abstrak

This study aims to determine the effect of Mn^{3+} and La^{3+} dopants on the structure of $PbBi_2Nb_2O_9$ (PBN) using atomistic simulation. PBN phase geometry is optimized before the phase is doped with Mn^{3+} and La^{3+}. Mn^{3+} partially substitutes octahedral Nb^{5+} in the perovskite layer. While La^{3+} partially substitute Bi^{3+} in the bismuth layer and dodecahedral Pb^{2+} in the perovskite layer. The concentration (x) of dopants that doped PBN is made in such a way that it produces a phase of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ (x = 0, 0.1, and 0.3) which is not charged. The simulation results show that the optimized PBN cell parameters are in a good agreement with the experimental result. Increasing the concentration of dopants result in the $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ phase (PBNM-Bi and PBNM-A) being less stable, as indicated by the increased lattice energy. PBNLM-Bi structures experiences an elongation which is 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

Aurivillius; $PbBi_2Nb_2O_9$; Atomistic simulation; Manganese and lanthanide dopants

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, Garg, Roy, & Verma, 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, Prijamboedi, Martoprawiro, & Ismunandar, 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 $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ (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 $PbBi_2Nb_2O_9$ (PBN) because it has ferroelectric properties. $PbBi_2Nb_2O_9$ has orthorhombic symmetry, *A21am* group space with $a = b =$ 5,496, and $c =$ 25.55 Å, 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, Kennedy, Gunawan, & Marsongkohadi, 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 $PbBi_2Nb_2O_9$ 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 A21am structures for $x = 0$, 0.1, 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, and 0.3). Therefore, this research looks for look for completion to explain these two things by means of atomistic simulation of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ ($x = 0.0$, 0.1, and 0.3) using the General Utility Lattice Program code.

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).

Simulations performed on the parent compound, namely: $PbBi_2Nb_2O_9$ (PBN). 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):

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

Where A_{ij}, ρ_{ij}, and C_{ij} are constants and ri 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):

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

Where $k_{\mathrm{i}}^{\mathrm{s}}$ 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):

$$\alpha_i = \sum \frac{(Yi\, e)^2}{k_i^s} \qquad (3)$$

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

Results and Discussion

$PbBi_2Nb_2O_9$ is a two-layer Aurivillius consisting of $(Bi_2O_2)^{2+}$ dan $(Pb_{n-1}Nb_nO_{3n+1})^{2-}$ 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 as shown in **Figure 1**. These orthorhombic compounds have a space group *A21am*, 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.

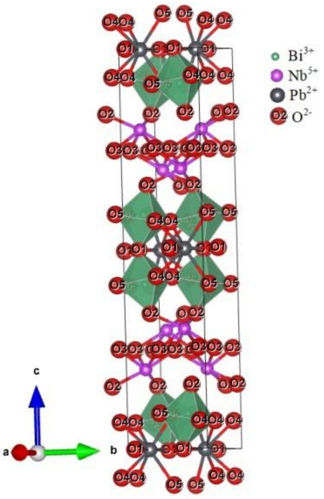


Figure 1. Crystal Structure of $PbBi_2Nb_2O_9$

The structural stability of $PbBi_2Nb_2O_9$ can be predicted by calculating the Goldschmidt perovskite tolerance formulated:

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

where r_A, r_B, and r_O are the ionic radii of cations A, B, and oxygen anions, respectively (Goldschmidt, 1926). Wendari et al. (2019) reported that the perovskite tolerance value calculated from $PbBi_2Nb_2O_9$ 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 $PbBi_2Nb_2O_9$ 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 egreement to the two layer Aurivillius of Bi_3TiNbO_9 reported by Rosyidah *et al.* (Rosyidah, Onggo, Khairurrijal, & Ismunandar, 2008). For simple compounds that are not layered structures, they can have much smaller lattice parameter differences (La Kilo, Umamah, & Laliyo, 2019).

Table 1. Parameter Cell of Calculated and Experimental $PbBi_2Nb_2O_9$

Parameter	Calculated	Exp.(Miura, 2002)	$\Delta_{(exp-calc)}$ (%)
c (Å)	5.4587	5.4960	0.68
b (Å)	5.3965	5.4960	1.81
c (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 $PbBi_2Nb_2O_9$ synthesis reported by Kim *et al*. (Kim, Hwang, & Lee, 2004). Cell parameters of *a*, *b,* and *c* are 5.503(4), 5.495(4), and 25.531(5), respectively. Aurivllius 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 $PbBi_2Nb_2O_9$ doping with La^{3+} and Mn^{3+}.

In this study, La^{3+} dopant can occupy Bi^{3+} of $(Bi_2O_2)^{2+}$ 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 $PbBi_{1.5}La_{0.5}Nb_2O_9$ ($x = 0.0$) where all La^{3+} occupies a layer of $(Bi_2O_2)^{2+}$ with an occupancy of 25% of 1 Bi occupancy. PBNLM-Bi-0.1 is $Pb_{0.8}Bi_{1.7}La_{0.5}Nb_{1.9}Mn_{0.1}O_9$, where $x = 0.1$, La^{3+} occupies 0.25% of Bi site in the $(Bi_2O_2)^{2+}$ 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 $Pb_{0.4}Bi_{2.1}La_{0.5}Nb_{1.7}Mn_{0.3}O_9$ ($x = 0.3$) where La^{3+} occupies 0.25% of the site of Bi^{3+} in the $(Bi_2O_2)^{2+}$ 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 $Pb_{0.8}La_{0.7}Bi_{1.5}Nb_{1.9}Mn_{0.1}O_9$ ($x = 0.1$), where La^{3+} occupies 25% of the Bi^{3+} site in the $(Bi_2O_2)^{2+}$ layer and 20% in Pb^{2+}; Mn 5% occupies the site of Nb^{5+} in the perovskite octahedral layer. PBNLM-A-0.3 is $Pb_{0.4}La_{1.1}Bi_{1.5}Nb_{1.7}Mn_{0.3}O_9$, where $x = 0.3$, La^{3+} occupies 0.25% of the Bi^{3+} site in the $(Bi_2O_2)^{2+}$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:

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

This tolerance involves partial substitution of cations A with A 'and / or B with B' 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).

Table 2. Perovskite Tolerance Factor of La^{3+} and Mn^{3+}-doped $PbBi_2Nb_2O_9$ Aurivillius Phase

Dopant composition (*x*)	Aurivillius	*t*	t^a
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	

[a] (Wendari et al., 2019)

The *t* value of this calculation is different from $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ 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 $(Bi_2O_2)^{2+}$.

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 $Pb_{0.8}Bi_{1.7}La_{0.5}Nb_{1.9}Mn_{0.1}O_9$ and $Pb_{0.4}Bi_{2.1}La_{0.5}Nb_{1.7}Mn_{0.3}O_9$ as they claim (Wendari et al., 2019).

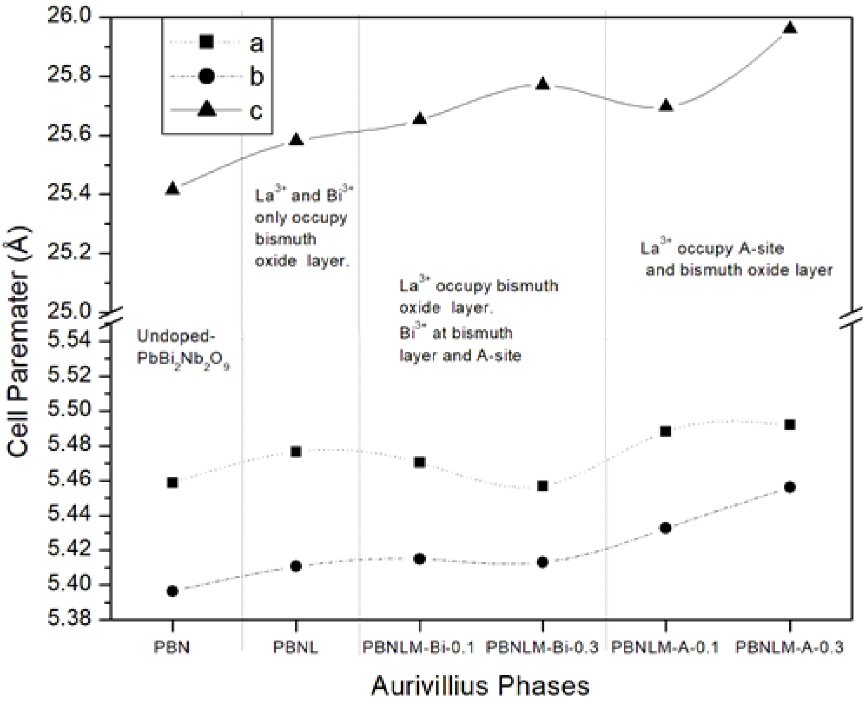


Figure 2. Lattice parameter of La^{3+} and Mn^{3+}-doped $PbBi_2Nb_2O_9$ Aurivillius Phase

The lattice parameter is also affected by the polarization of ions. In this study, the polarization strength of cations is $Bi^{3+}>Nb^{5+}>Pb^{2+}$. 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 $SrBi_2(Ta_{1-x}Nb_x)_2O_9$ 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 1.**

Table 3. Interatomic potential of $PbBi_2Nb_2O_9$ and $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$

	A (eV)	*ρ* (Å)	*C* (eV Å)
a) Buckingham			
short range			
b...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	

Based on **Table 3**, the repulsive force between cationic and anionic shells is Bi...O>Pb...O>Nb...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 $ABi_4Ti_4O_{15}$ (A = Ba, Ca, Sr, 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).

$PbBi_2Nb_2O_9$ lattice energy is much smaller than the Bi_3TiNbO_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 Aurivillus which in theory will have more energy than the

Aurivilius lattice energy with the octahedral layer above it. But these results are contrary to what is expected. In fact, $PbBi_2Nb_2O_9$ has a lower lattice energy compared to the four layer Aurivillius lattice energy of $BaBi_4Ti_4O_{15}$ (-770.64590 eV) and $Ba_2Bi_4Ti_5O_{18}$ (-927.2781 eV), which means that the $PbBi_2Nb_2O_9$ lattice energy is very stable so it is not surprising if many researchers try to modify this structure as a potential as ferroelectromagnetic material in industry. When $PbBi_2Nb_2O_9$ is doped with La^{3+} and Mn^{3+}, the resulting Aurivillius lattice energy are becomes greater as shown in **Figure 3**.

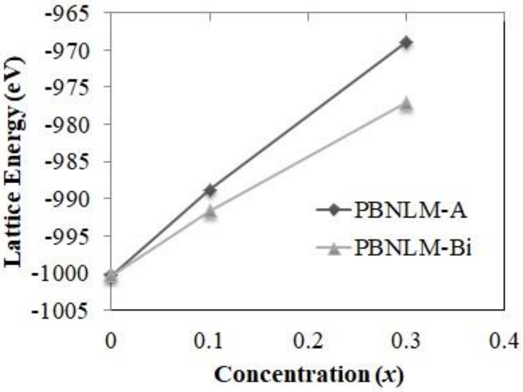


Figure 3. Lattice Energy of Mn^{3+} and La^{3+}-doped $PbBi_2Nb_2O_9$

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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ 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).

Conclusion

The atomistic simulation results are in good agreement with the experimental results based on the lattice parameters of the parent compound, $PbBi_2Nb_2O_9$. Bi^{3+} which partially substitutes Pb2+ in the perovskite layer causes the structure of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ ($x = 0$, 0.1, and 0.3) to elongate. Conversely, if Pb^{2+} is substituted by La^{3+} then that elongation does 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 $PbBi_2Nb_2O_9$ phase being less stable. PBNLM-Bi is more easily synthesized compared to PBNLM-A.

References

Aurivillius, B. (1949a). Mixed Bismuth Oxides with Layer lattices: I The Structure Type of CaBi2Nb2O9. *Arkiv Kemi Band I*.

Aurivillius, B. (1949b). Mixed bismuth oxides with layer lattices. II. Structure of Bi4Ti3O12. *Arkiv for Kemi*.

Born, M., & Mayer, J. E. (1932). Zur Gittertheorie der Ionenkristalle. *Zeitschrift Für Physik*. https://doi.org/10.1007/BF01340511

Gale, J. D. (1997). GULP: A computer program for the symmetry-adapted simulation of solids. *Journal of the Chemical Society - Faraday Transactions*. https://doi.org/10.1039/a606455h

Gale, J. D., & Rohl, A. L. (2003). The General Utility Lattice Program (GULP). *Molecular Simulation*. https://doi.org/10.1080/0892702031000104887

Goldschmidt, V. M. (1926). Die gesetze der krystallochemie. *Naturwissenschaften*, *14*(21), 477–485.

Ismunandar, Kennedy, B. J., Gunawan, & Marsongkohadi. (1996). Structure of ABi2Nb2O9 (A = Sr, Ba): Refinement of powder neutron diffraction data. *Journal of Solid State Chemistry*. https://doi.org/10.1006/jssc.1996.0321

Kilo, A. La, Prijamboedi, B., Martoprawiro, M. A., & Ismunandar. (2011). Modeling ionic conduction in γ-Bi 2VO 5.5. *Proceedings - International Conference on Instrumentation, Communication, Information Technology and Biomedical Engineering 2011, ICICI-BME 2011*. https://doi.org/10.1109/ICICI-BME.2011.6108652

Kim, H. G., Hwang, D. W., & Lee, J. S. (2004). An undoped, single-phase oxide photocatalyst working under visible light. *Journal of the American Chemical Society*. https://doi.org/10.1021/ja049676a

La Kilo, A., Costanzo, A., Mazza, D., Martoprawiro, M. A., Prijamboedi, B., & Ismunandar, I. (2020). Highest ionic conductivity of BIMEVOX (ME = 10% Cu, 10%

Ga, 20% Ta): Computational modeling and simulation. *Indonesian Journal of Chemistry*, *20*(3), 510. https://doi.org/10.22146/ijc.42635

La Kilo, A., & Mazza, D. (2011). Pemodelan konduktivitas ion dalam struktur Li2sc3(PO4)3 (Modeling ionic conductivity in Li2sc3(PO4)3 structure). *Jurnal Manusia Dan Lingkungan*, *18*(3), 179–183. https://doi.org/https://doi.org/10.22146/jml.18439

La Kilo, A., Umamah, T. S., & Laliyo, L. A. R. (2019). Study on the Stability of Trivalent Cations Doped Zirconia through Atomistic Modeling. *Jurnal Kimia Sains Dan Aplikasi*, *22*(4), 129–135. https://doi.org/10.14710/jksa.22.4.129-135

Miura, K. (2002). Electronic properties of ferroelectric SrBi2Ta2O 9, SrBi2Nb2O9, and PbBi 2Nb2O9 with optimized structures. *Applied Physics Letters*. https://doi.org/10.1063/1.1474607

Prakash, P., Garg, A., Roy, M. K., & Verma, H. C. (2007). Novel low-temperature synthesis of ferroelectric neodymium-doped bismuth titanate nanoparticles. *Journal of the American Ceramic Society*. https://doi.org/10.1111/j.1551-2916.2007.01539.x

Rosyidah, A., Onggo, D., Khairurrijal, & Ismunandar. (2008). Atomic simulations of Aurivillius oxides: Bi3TiNbO9, Bi4Ti3O12, BaBi4Ti4O 15 and Ba2Bi4Ti5O18 doped with Pb, Al, Ga, In, Ta. *Journal of the Chinese Chemical Society*. https://doi.org/10.1002/jccs.200800018

Sadapu, S. (2015). Pengaruh Subtitusi Bi secara Parsial oleh Dopan (A= Ba, Ca, Sr dan Pb) dalam Lapisan [Bi2O2] 2+ pada Oksida Aurivillius ABi4Ti4O15. *Skripsi*, *1*(441410014).

Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*. https://doi.org/10.1107/S0567739476001551

Shimakawa, Y., Kubo, Y., Tauchi, Y., Kamiyama, T., Asano, H., & Izumi, F. (2000). Structural distortion and ferroelectric properties of SrBi2(Ta1-xNbx)2O9. *Applied Physics Letters*. https://doi.org/10.1063/1.1319509

Wendari, T. P., Arief, S., Mufti, N., Suendo, V., Prasetyo, A., Ismunandar, … Zulhadjri.

(2019). Synthesis, structural analysis and dielectric properties of the double-layer Aurivillius compound Pb1-2xBi1.5+2xLa0.5Nb2-xMnxO9. *Ceramics International*, *45*(44), 17276–17282. https://doi.org/10.1016/j.ceramint.2019.05.285

Atomistic Simulation of La and Mn-Doped $PbBi_2Nb_2O_9$ Aurivillius Phase

Akram La Kilo[1,2], Ramona Nintias R. Abas[1], Alberto Costanzo[3], Daniele Mazza[3], Deasy N. Botutihe[1,2], Jafar La Kilo [1,2]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, State University of Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bonebolango Gorontalo, 96554, Indonesia

[2]Department of Educational Chemistry, Faculty of Mathematics and Natural Sciences, State University of Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bonebolango Gorontalo, 96554, Indonesia

[3]Dipartimento di Scienza dei Materiali e' Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

Correspondence: E-mail: akram@ung.ac.id

Abstrak

This study aims to determine the effect of Mn^{3+} and La^{3+} dopants on the structure of $PbBi_2Nb_2O_9$ (PBN) using atomistic simulation. PBN phase geometry is optimized before the phase is doped with Mn^{3+} and La^{3+}. Mn^{3+} partially substitutes octahedral Nb^{5+} in the perovskite layer. While La^{3+} partially substitute Bi^{3+} in the bismuth layer and dodecahedral Pb^{2+} in the perovskite layer. The concentration (x) of dopants that doped PBN is made in such a way that it produces a phase of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ ($x = 0, 0.1$, and 0.3) which is not charged. The simulation results show that the optimized PBN cell parameters are in a good agreement with the experimental result. Increasing the concentration of dopants result in the $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ phase (PBNM-Bi and PBNM-A) being less stable, as indicated by the increased lattice energy. PBNLM-Bi structures experiences an elongation which is 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

Aurivillius; $PbBi_2Nb_2O_9$; Atomistic simulation; Manganese and lanthanide dopants

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, Garg, Roy, & Verma, 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, Prijamboedi, Martoprawiro, & Ismunandar, 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 $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ (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 $PbBi_2Nb_2O_9$ (PBN) because it has ferroelectric properties. $PbBi_2Nb_2O_9$ has orthorhombic symmetry, *A21am* group space with $a = b = 5{,}496$, and $c = 25.55$ Å, 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, Kennedy, Gunawan, & Marsongkohadi, 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 $PbBi_2Nb_2O_9$ 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 A21am structures for $x = 0$, 0.1, 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, and 0.3). Therefore, this research looks for look for completion to explain these two things by means of atomistic simulation of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ ($x = 0.0$, 0.1, and 0.3) using the General Utility Lattice Program code.

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).

Simulations performed on the parent compound, namely: $PbBi_2Nb_2O_9$ (PBN). 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):

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

Where A_{ij}, ρ_{ij}, and C_{ij} are constants and ri 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):

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

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):

$$\alpha_i = \sum \frac{(Yi\,e)^2}{k_i^s} \qquad (3)$$

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

Results and Discussion

$PbBi_2Nb_2O_9$ is a two-layer Aurivillius consisting of $(Bi_2O_2)^{2+}$ dan $(Pb_{n-1}Nb_nO_{3n+1})^{2-}$ 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 as shown in **Figure 1**. These orthorhombic compounds have a space group *A21am*, 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.

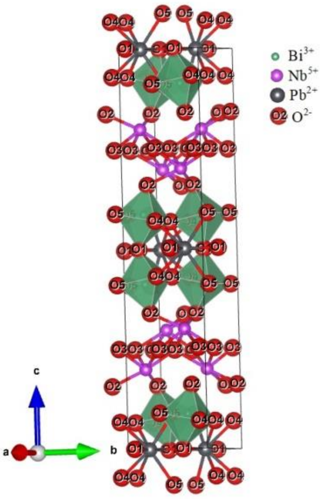


Figure 1. Crystal Structure of $PbBi_2Nb_2O_9$

The structural stability of $PbBi_2Nb_2O_9$ can be predicted by calculating the Goldschmidt perovskite tolerance formulated:

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

where r_A, r_B, and r_O are the ionic radii of cations A, B, and oxygen anions, respectively (Goldschmidt, 1926). Wendari et al. (2019) reported that the perovskite tolerance value calculated from $PbBi_2Nb_2O_9$ 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 $PbBi_2Nb_2O_9$ 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 egreement to the two layer Aurivillius of Bi_3TiNbO_9 reported by Rosyidah *et al.* (Rosyidah, Onggo, Khairurrijal, & Ismunandar, 2008). For simple compounds that are not layered structures, they can have much smaller lattice parameter differences (La Kilo, Umamah, & Laliyo, 2019).

Table 1. Parameter Cell of Calculated and Experimental $PbBi_2Nb_2O_9$

Parameter	Calculated	Exp.(Miura, 2002)	$\Delta_{(exp-calc)}$ (%)
c (Å)	5.4587	5.4960	0.68
b (Å)	5.3965	5.4960	1.81
c (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 $PbBi_2Nb_2O_9$ synthesis reported by Kim *et al.* (Kim, Hwang, & Lee, 2004). Cell parameters of *a*, *b,* and *c* are 5.503(4), 5.495(4), and 25.531(5), respectively. Aurivllius 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 $PbBi_2Nb_2O_9$ doping with La^{3+} and Mn^{3+}.

In this study, La^{3+} dopant can occupy Bi^{3+} of $(Bi_2O_2)^{2+}$ 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 $PbBi_{1.5}La_{0.5}Nb_2O_9$ ($x = 0.0$) where all La^{3+} occupies a layer of $(Bi_2O_2)^{2+}$ with an occupancy of 25% of 1 Bi occupancy. PBNLM-Bi-0.1 is $Pb_{0.8}Bi_{1.7}La_{0.5}Nb_{1.9}Mn_{0.1}O_9$, where $x = 0.1$, La^{3+} occupies 0.25% of Bi site in the $(Bi_2O_2)^{2+}$ 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 $Pb_{0.4}Bi_{2.1}La_{0.5}Nb_{1.7}Mn_{0.3}O_9$ ($x = 0.3$) where La^{3+} occupies 0.25% of the site of Bi^{3+} in the $(Bi_2O_2)^{2+}$ 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 $Pb_{0.8}La_{0.7}Bi_{1.5}Nb_{1.9}Mn_{0.1}O_9$ ($x = 0.1$), where La^{3+} occupies 25% of the Bi^{3+} site in the $(Bi_2O_2)^{2+}$ layer and 20% in Pb^{2+}; Mn 5% occupies the site of Nb^{5+} in the perovskite octahedral layer. PBNLM-A-0.3 is $Pb_{0.4}La_{1.1}Bi_{1.5}Nb_{1.7}Mn_{0.3}O_9$, where $x = 0.3$, La^{3+} occupies 0.25% of the Bi^{3+} site in the $(Bi_2O_2)^{2+}$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:

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

This tolerance involves partial substitution of cations A with A 'and / or B with B' 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).

Table 2. Perovskite Tolerance Factor of La^{3+} and Mn^{3+}-doped $PbBi_2Nb_2O_9$ Aurivillius Phase

Dopant composition (x)	Aurivillius	t	t^a
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	

[a] (Wendari et al., 2019)

The t value of this calculation is different from $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ 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 $(Bi_2O_2)^{2+}$.

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 $Pb_{0.8}Bi_{1.7}La_{0.5}Nb_{1.9}Mn_{0.1}O_9$ and $Pb_{0.4}Bi_{2.1}La_{0.5}Nb_{1.7}Mn_{0.3}O_9$ as they claim (Wendari et al., 2019).

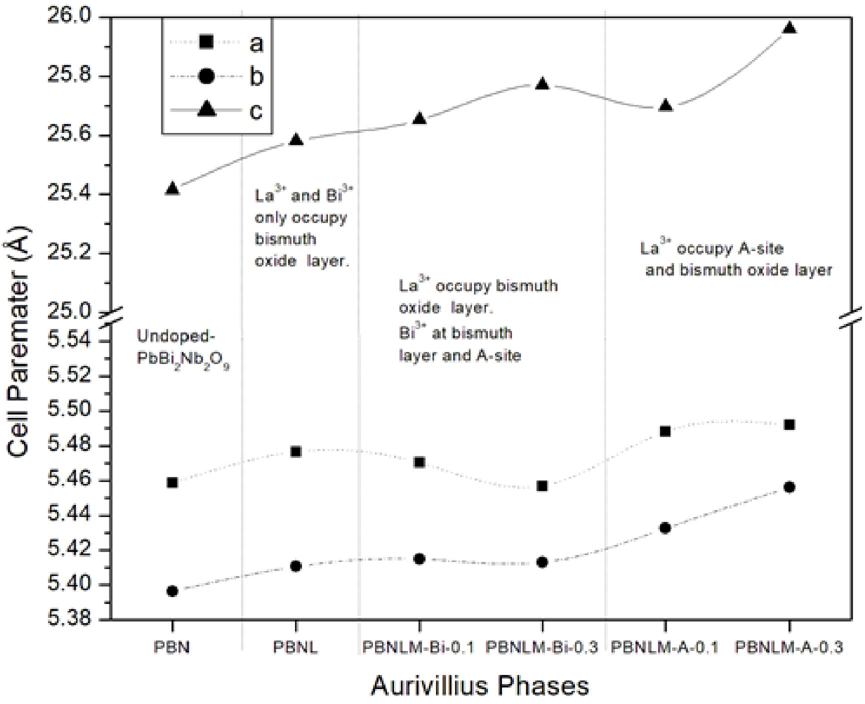


Figure 2. Lattice parameter of La^{3+} and Mn^{3+}-doped $PbBi_2Nb_2O_9$ Aurivillius Phase

The lattice parameter is also affected by the polarization of ions. In this study, the polarization strength of cations is $Bi^{3+}>Nb^{5+}>Pb^{2+}$. 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 $SrBi_2(Ta_{1-x}Nb_x)_2O_9$ 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 1.**

Table 3. Interatomic potential of $PbBi_2Nb_2O_9$ and $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$

	A (eV)	*ρ* (Å)	*C* (eV Å)
a) Buckingham			
short range			
b...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	

Based on **Table 3**, the repulsive force between cationic and anionic shells is Bi...O>Pb...O>Nb...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 $ABi_4Ti_4O_{15}$ (A = Ba, Ca, Sr, 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).

$PbBi_2Nb_2O_9$ lattice energy is much smaller than the Bi_3TiNbO_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 Aurivillus which in theory will have more energy than the

Aurivilius lattice energy with the octahedral layer above it. But these results are contrary to what is expected. In fact, $PbBi_2Nb_2O_9$ has a lower lattice energy compared to the four layer Aurivillius lattice energy of $BaBi_4Ti_4O_{15}$ (-770.64590 eV) and $Ba_2Bi_4Ti_5O_{18}$ (-927.2781 eV), which means that the $PbBi_2Nb_2O_9$ lattice energy is very stable so it is not surprising if many researchers try to modify this structure as a potential as ferroelectromagnetic material in industry. When $PbBi_2Nb_2O_9$ is doped with La^{3+} and Mn^{3+}, the resulting Aurivillius lattice energy are becomes greater as shown in **Figure 3**.

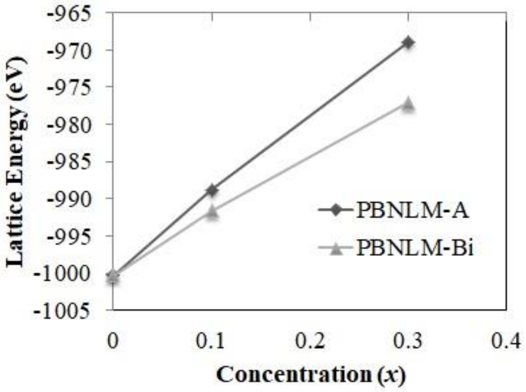


Figure 3. Lattice Energy of Mn^{3+} and La^{3+}-doped $PbBi_2Nb_2O_9$

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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ 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).

Conclusion

The atomistic simulation results are in good agreement with the experimental results based on the lattice parameters of the parent compound, $PbBi_2Nb_2O_9$. Bi^{3+} which partially substitutes Pb2+ in the perovskite layer causes the structure of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ ($x = 0$, 0.1, and 0.3) to elongate. Conversely, if Pb^{2+} is substituted by La^{3+} then that elongation does 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 $PbBi_2Nb_2O_9$ phase being less stable. PBNLM-Bi is more easily synthesized compared to PBNLM-A.

References

Aurivillius, B. (1949a). Mixed Bismuth Oxides with Layer lattices: I The Structure Type of CaBi2Nb2O9. *Arkiv Kemi Band I*.

Aurivillius, B. (1949b). Mixed bismuth oxides with layer lattices. II. Structure of Bi4Ti3O12. *Arkiv for Kemi*.

Born, M., & Mayer, J. E. (1932). Zur Gittertheorie der Ionenkristalle. *Zeitschrift Für Physik*. https://doi.org/10.1007/BF01340511

Gale, J. D. (1997). GULP: A computer program for the symmetry-adapted simulation of solids. *Journal of the Chemical Society - Faraday Transactions*. https://doi.org/10.1039/a606455h

Gale, J. D., & Rohl, A. L. (2003). The General Utility Lattice Program (GULP). *Molecular Simulation*. https://doi.org/10.1080/0892702031000104887

Goldschmidt, V. M. (1926). Die gesetze der krystallochemie. *Naturwissenschaften*, *14*(21), 477–485.

Ismunandar, Kennedy, B. J., Gunawan, & Marsongkohadi. (1996). Structure of ABi2Nb2O9 (A = Sr, Ba): Refinement of powder neutron diffraction data. *Journal of Solid State Chemistry*. https://doi.org/10.1006/jssc.1996.0321

Kilo, A. La, Prijamboedi, B., Martoprawiro, M. A., & Ismunandar. (2011). Modeling ionic conduction in γ-Bi 2VO 5.5. *Proceedings - International Conference on Instrumentation, Communication, Information Technology and Biomedical Engineering 2011, ICICI-BME 2011*. https://doi.org/10.1109/ICICI-BME.2011.6108652

Kim, H. G., Hwang, D. W., & Lee, J. S. (2004). An undoped, single-phase oxide photocatalyst working under visible light. *Journal of the American Chemical Society*. https://doi.org/10.1021/ja049676a

La Kilo, A., Costanzo, A., Mazza, D., Martoprawiro, M. A., Prijamboedi, B., & Ismunandar, I. (2020). Highest ionic conductivity of BIMEVOX (ME = 10% Cu, 10%

Ga, 20% Ta): Computational modeling and simulation. *Indonesian Journal of Chemistry*, *20*(3), 510. https://doi.org/10.22146/ijc.42635

La Kilo, A., & Mazza, D. (2011). Pemodelan konduktivitas ion dalam struktur Li2sc3(PO4)3 (Modeling ionic conductivity in Li2sc3(PO4)3 structure). *Jurnal Manusia Dan Lingkungan*, *18*(3), 179–183. https://doi.org/https://doi.org/10.22146/jml.18439

La Kilo, A., Umamah, T. S., & Laliyo, L. A. R. (2019). Study on the Stability of Trivalent Cations Doped Zirconia through Atomistic Modeling. *Jurnal Kimia Sains Dan Aplikasi*, *22*(4), 129–135. https://doi.org/10.14710/jksa.22.4.129-135

Miura, K. (2002). Electronic properties of ferroelectric SrBi2Ta2O 9, SrBi2Nb2O9, and PbBi 2Nb2O9 with optimized structures. *Applied Physics Letters*. https://doi.org/10.1063/1.1474607

Prakash, P., Garg, A., Roy, M. K., & Verma, H. C. (2007). Novel low-temperature synthesis of ferroelectric neodymium-doped bismuth titanate nanoparticles. *Journal of the American Ceramic Society*. https://doi.org/10.1111/j.1551-2916.2007.01539.x

Rosyidah, A., Onggo, D., Khairurrijal, & Ismunandar. (2008). Atomic simulations of Aurivillius oxides: Bi3TiNbO9, Bi4Ti3O12, BaBi4Ti4O 15 and Ba2Bi4Ti5O18 doped with Pb, Al, Ga, In, Ta. *Journal of the Chinese Chemical Society*. https://doi.org/10.1002/jccs.200800018

Sadapu, S. (2015). Pengaruh Subtitusi Bi secara Parsial oleh Dopan (A= Ba, Ca, Sr dan Pb) dalam Lapisan [Bi2O2] 2+ pada Oksida Aurivillius ABi4Ti4O15. *Skripsi*, *1*(441410014).

Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*. https://doi.org/10.1107/S0567739476001551

Shimakawa, Y., Kubo, Y., Tauchi, Y., Kamiyama, T., Asano, H., & Izumi, F. (2000). Structural distortion and ferroelectric properties of SrBi2(Ta1-xNbx)2O9. *Applied Physics Letters*. https://doi.org/10.1063/1.1319509

Wendari, T. P., Arief, S., Mufti, N., Suendo, V., Prasetyo, A., Ismunandar, … Zulhadjri.

(2019). Synthesis, structural analysis and dielectric properties of the double-layer Aurivillius compound Pb1-2xBi1.5+2xLa0.5Nb2-xMnxO9. *Ceramics International*, *45*(44), 17276–17282. https://doi.org/10.1016/j.ceramint.2019.05.285

Atomistic Simulation of La and Mn-Doped $PbBi_2Nb_2O_9$ Aurivillius Phase

Akram La Kilo[1,2], Ramona Nintias R. Abas[1], Alberto Costanzo[3], Daniele Mazza[3], Deasy N. Botutihe[1,2], Jafar La Kilo [1,2]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, ~~State University of Gorontalo~~Universitas Negeri Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bone Bolango Gorontalo, 96554, Indonesia

[2]Department of Educational Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Gorontalo~~State University of Gorontalo~~, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bonebolango Gorontalo, 96554, Indonesia

[3]Dipartimento di Scienza dei Materiali e' Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

Correspondence: E-mail: akram@ung.ac.id

Abstrak

This study aims to determine the effect of Mn^{3+} and La^{3+} dopants on the structure of $PbBi_2Nb_2O_9$ (PBN) using atomistic simulation. PBN phase geometry is optimized before the phase is doped with Mn^{3+} and La^{3+}. Mn^{3+} partially substitutes octahedral Nb^{5+} in the perovskite layer. While La^{3+} partially substitute Bi^{3+} in the bismuth layer and dodecahedral Pb^{2+} in the perovskite layer. The concentration (x) of dopants that doped PBN is made in such a way that it produces a phase of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ (x = 0, 0.1, and 0.3) which is not charged. The simulation results show that the optimized PBN cell parameters are in a good agreement with the experimental result. Increasing the concentration of dopants result in the $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ phase (PBNM-Bi and PBNM-A) being less stable, as indicated by the increased lattice energy. PBNLM-Bi structures experiences an elongation which is 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

Aurivillius; $PbBi_2Nb_2O_9$; Atomistic simulation; Manganese and lanthanide dopants

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 $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ (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 $PbBi_2Nb_2O_9$ (PBN) because it has ferroelectric properties. $PbBi_2Nb_2O_9$ has orthorhombic symmetry, *A21am* group space with $a = b = 5{,}496$, and $c = 25.55$ Å, 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 A~~a~~urivillius $PbBi_2Nb_2O_9$ 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 A21am structures for $x = 0$, 0.1, 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, and 0.3). Therefore, this research ~~looks for~~ look for completion to explain these two things by means of atomistic simulation of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ ($x = 0.0$, 0.1, 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).

Formatted: English (United States)

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).

Formatted: English (United States)

The parent compound that was simulated was $PbBi_2Nb_2O_9$ (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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ ($x = 0.0$, 0.1, 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 optimiser and BFGS hessian update, and the results were declared convergent if the Gnormal value was less than 0.01.~~Simulations performed on the parent compound, namely: $PbBi_2Nb_2O_9$ (PBN).~~

Formatted: Superscript

Formatted: Superscript

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):

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

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):

Formatted: Font: Italic

Formatted: Subscript

$$U_3 = \sum_i k_i^s \, r_i^2 \qquad (2)$$

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):

$$\alpha_i = \sum \frac{(Yi\ e)^2}{k_i^s} \qquad (3)$$

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

In addition to the lattice energy generated from the atomistic simulation, ~~The~~ structural stability of $PbBi_2Nb_2O_9$ can be predicted by calculating the Goldschmidt perovskite tolerance formulated:

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

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

Formatted: English (United States)

Results and Discussion

$PbBi_2Nb_2O_9$ is a two-layer Aurivillius consisting of $(Bi_2O_2)^{2+}$ dan $(Pb_{n-1}Nb_nO_{3n+1})^{2-}$ 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 as shown in **Figure 1~~Figure 1~~**. These

Formatted: Indonesian

orthorhombic compounds have a space group *A21am*, 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.

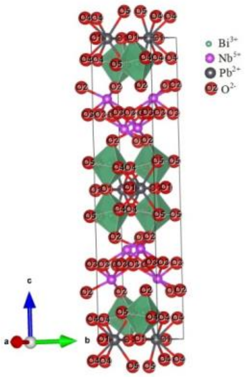


Figure 1. Crystal Structure of $PbBi_2Nb_2O_9$

~~The structural stability of $PbBi_2Nb_2O_9$ can be predicted by calculating the Goldschmidt perovskite tolerance formulated:~~

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

~~where r_A, r_B, and r_O are the ionic radii of cations A, B, and oxygen anions, respectively (Goldschmidt, 1926)~~. Wendari et al. (2019) reported that the perovskite tolerance value calculated from $PbBi_2Nb_2O_9$ 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.

Formatted: Font: Italic

Formatted: Font: Italic

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 $PbBi_2Nb_2O_9$ 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**~~**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 egreement to the two layer Aurivillius of Bi_3TiNbO_9 reported by~~ Rosyidah *et al*~~. ~~(~~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).

Formatted: English (United Kingdom)

Table 1. Parameter Cell of Calculated and Experimental $PbBi_2Nb_2O_9$

Parameter	Calculated	Exp.(Miura, 2002)	$\Delta_{(exp\text{-}calc)}$ (%)
c (Å)	5.4587	5.4960	0.68
b (Å)	5.3965	5.4960	1.81
c (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 $PbBi_2Nb_2O_9$ synthesis reported by ~~Kim *et al*. (~~Kim et al.~~,~~ (2004). Cell parameters of *a*, *b*, and *c* are 5.503(4), 5.495(4), and 25.531(5), respectively. Aurivllius 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 $PbBi_2Nb_2O_9$ doping with La^{3+} and Mn^{3+}.

In this study, La^{3+} dopant can occupy Bi^{3+} of $(Bi_2O_2)^{2+}$ 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 $PbBi_{1.5}La_{0.5}Nb_2O_9$ ($x = 0.0$) where all La^{3+} occupies a layer of $(Bi_2O_2)^{2+}$ with an occupancy of 25% of 1 Bi occupancy. PBNLM-Bi-0.1 is $Pb_{0.8}Bi_{1.7}La_{0.5}Nb_{1.9}Mn_{0.1}O_9$, where $x = 0.1$, La^{3+} occupies 0.25% of Bi site in the $(Bi_2O_2)^{2+}$ 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 $Pb_{0.4}Bi_{2.1}La_{0.5}Nb_{1.7}Mn_{0.3}O_9$ ($x = 0.3$) where La^{3+} occupies 0.25% of the site of Bi^{3+} in the $(Bi_2O_2)^{2+}$ 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 $Pb_{0.8}La_{0.7}Bi_{1.5}Nb_{1.9}Mn_{0.1}O_9$ ($x = 0.1$), where La^{3+} occupies 25% of the Bi^{3+} site in the $(Bi_2O_2)^{2+}$ layer and 20% in Pb^{2+}; Mn 5% occupies the site of Nb^{5+} in the perovskite octahedral layer. PBNLM-A-0.3 is $Pb_{0.4}La_{1.1}Bi_{1.5}Nb_{1.7}Mn_{0.3}O_9$, where $x = 0.3$, La^{3+} occupies 0.25% of the Bi^{3+} site in the $(Bi_2O_2)^{2+}$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:

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

This tolerance involves partial substitution of cations A with A 'and / or B with B' 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**~~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

Formatted: Font: Bold

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).

Table 2. Perovskite Tolerance Factor of La^{3+} and Mn^{3+}-doped $PbBi_2Nb_2O_9$ Aurivillius Phase

Dopant composition (x)	Aurivillius	t	t^a
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	

[a](Wendari et al., 2019)

The t value of this calculation is different from $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ 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 $(Bi_2O_2)^{2+}$.

Simulation results of the compounds are shown in **Figure 2**~~**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 $Pb_{0.8}Bi_{1.7}La_{0.5}Nb_{1.9}Mn_{0.1}O_9$ and $Pb_{0.4}Bi_{2.1}La_{0.5}Nb_{1.7}Mn_{0.3}O_9$ as they claim (Wendari et al., 2019).

Formatted: Check spelling and grammar

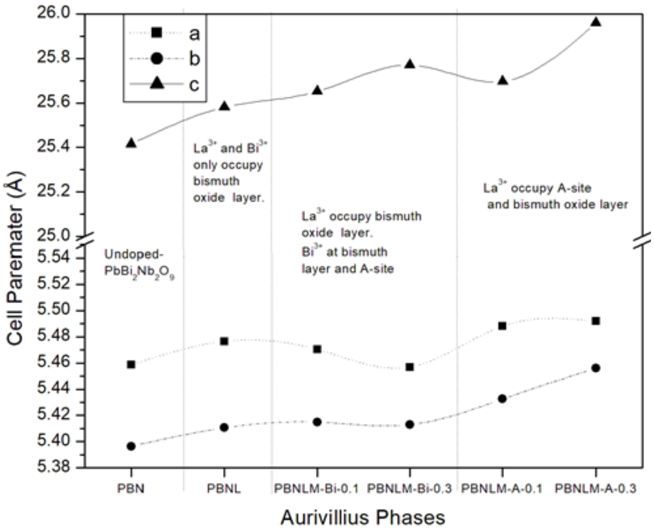


Figure 2. Lattice parameter of La^{3+} and Mn^{3+}-doped $PbBi_2Nb_2O_9$ Aurivillius Phase

The lattice parameter is also affected by the polarization of ions. In this study, the polarization strength of cations is $Bi^{3+}>Nb^{5+}>Pb^{2+}$. 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 $SrBi_2(Ta_{1-x}Nb_x)_2O_9$ 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 1Table 3~~Table 2~~**.

Table 3. Interatomic potential of $PbBi_2Nb_2O_9$ and $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$

	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* (eVÅ²)	Shell (e)	

Formatted: English (United Kingdom)

Formatted: English (United Kingdom)

Pb^{2+}	205.00	1.00
Nb^{5+}	1358.58	-4.497
Bi^{3+}	359.55	-5.51
O^{2-}	6.3	-2.04

Based on **Table 3**~~**Table 2**~~, the repulsive force between cationic and anionic shells is Bi...O>Pb...O>Nb...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 $ABi_4Ti_4O_{15}$ (A = Ba, Ca, Sr, 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).

Formatted: English (United Kingdom)

$PbBi_2Nb_2O_9$ lattice energy is much smaller than the Bi_3TiNbO_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 Aurivillus which in theory will have more energy than the Aurivilius lattice energy with the octahedral layer above it. But these results are contrary to what is expected. In fact, $PbBi_2Nb_2O_9$ has a lower lattice energy compared to the four layer Aurivillius lattice energy of $BaBi_4Ti_4O_{15}$ (-770.64590 eV) and $Ba_2Bi_4Ti_5O_{18}$ (-927.2781 eV), which means that the $PbBi_2Nb_2O_9$ lattice energy is very stable so it is not surprising if many researchers try to modify this structure as a potential as ferroelectromagnetic material in industry. When $PbBi_2Nb_2O_9$ is doped with La^{3+} and Mn^{3+}, the resulting Aurivillius lattice energy are becomes greater as shown in **Figure 3**~~**Figure 3**~~.

Formatted: Font: (Default) Times New Roman, English (United Kingdom)

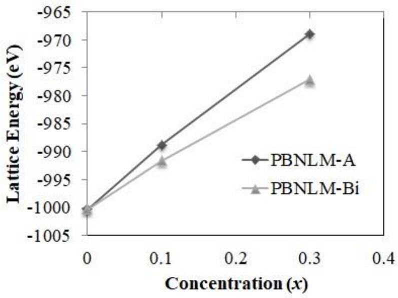


Figure 3~~3~~. Lattice Energy of Mn^{3+} and La^{3+}-doped $PbBi_2Nb_2O_9$

Formatted: Font: (Default) Times New Roman, Bold, (Asian) Japanese

Formatted: Font: (Default) Times New Roman, Bold, (Asian) Japanese

Formatted: Font: (Default) Times New Roman, (Asian) Japanese

Formatted: Font: (Default) Times New Roman

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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ 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 position B and in small amounts, partially substitutes Nb5+ which carries ferroelectric properties. Mn^{3+} which has four unpaired electrons in the *d* orbital causes Aurivellius to also have magnetic properties. These nonspherical *d* orbital add to the octahedral distortion of the perovskite layer.

Formatted: Superscript

Formatted: Superscript

Formatted: Superscript

Formatted: Superscript

Formatted: Font: Italic

Formatted: Font: Italic

Conclusion

The atomistic simulation results are in good agreement with the experimental results based on the lattice parameters of the parent compound, $PbBi_2Nb_2O_9$. Bi^{3+} which partially substitutes Pb^{2+} in the perovskite layer causes the structure of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ (x = 0, 0.1, and 0.3) to elongate. Conversely, if Pb^{2+} is substituted by La^{3+} then that elongation does 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

Formatted: Superscript

Mn^{3+} and La^{3+}-doped $PbBi_2Nb_2O_9$ phase being less stable. PBNLM-Bi is predicted more easily synthesized compared to PBNLM-A.

References

Aurivillius, B. (1949a). Mixed Bismuth Oxides with Layer lattices: I The Structure Type of CaBi2Nb2O9. *Arkiv Kemi Band I*.

Aurivillius, B. (1949b). Mixed bismuth oxides with layer lattices. II. Structure of Bi4Ti3O12. *Arkiv for Kemi*.

Born, M., & Mayer, J. E. (1932). Zur Gittertheorie der Ionenkristalle. *Zeitschrift Für Physik*. https://doi.org/10.1007/BF01340511

Dutra, J. D. L., Bispo, T. D., de Freitas, S. M., & dos S. Rezende, M. V. (2021). ParamGULP: An efficient Python code for obtaining interatomic potential parameters for General Utility Lattice Program. *Computer Physics Communications*, *265*, 107996. https://doi.org/https://doi.org/10.1016/j.cpc.2021.107996

Gale, J. D. (1997). GULP: A computer program for the symmetry-adapted simulation of solids. *Journal of the Chemical Society - Faraday Transactions*. https://doi.org/10.1039/a606455h

Gale, J. D., & Rohl, A. L. (2003). The General Utility Lattice Program (GULP). *Molecular Simulation*. https://doi.org/10.1080/0892702031000104887

Goldschmidt, V. M. (1926). Die gesetze der krystallochemie. *Naturwissenschaften*, *14*(21), 477–485.

Islam, M. S., Lazure, S., Vannier, R., Nowogrocki, G., & Mairesse, G. (1998). Structural and computational studies of Bi 2 WO 6 based oxygen ion conductors. *Journal of Materials Chemistry*, *8*(3), 655–660.

Ismunandar, Kennedy, B. J., Gunawan, & Marsongkohadi. (1996). Structure of ABi2Nb2O9 (A = Sr, Ba): Refinement of powder neutron diffraction data. *Journal of Solid State Chemistry*. https://doi.org/10.1006/jssc.1996.0321

Kilo, A. La, Prijamboedi, B., Martoprawiro, M. A., & Ismunandar. (2011). Modeling ionic conduction in γ-Bi 2VO 5.5. *Proceedings - International Conference on Instrumentation, Communication, Information Technology and Biomedical*

Engineering 2011, ICICI-BME 2011. https://doi.org/10.1109/ICICI-BME.2011.6108652

Kim, H. G., Hwang, D. W., & Lee, J. S. (2004). An undoped, single-phase oxide photocatalyst working under visible light. *Journal of the American Chemical Society*. https://doi.org/10.1021/ja049676a

La Kilo, A., Costanzo, A., Mazza, D., Martoprawiro, M. A., Prijamboedi, B., & Ismunandar, I. (2020). Highest ionic conductivity of BIMEVOX (ME = 10% Cu, 10% Ga, 20% Ta): Computational modeling and simulation. *Indonesian Journal of Chemistry*, *20*(3), 510. https://doi.org/10.22146/ijc.42635

La Kilo, A., & Mazza, D. (2011). Pemodelan konduktivitas ion dalam struktur Li2sc3(PO4)3 (Modeling ionic conductivity in Li2sc3(PO4)3 structure). *Jurnal Manusia Dan Lingkungan*, *18*(3), 179–183. https://doi.org/https://doi.org/10.22146/jml.18439

La Kilo, A., Umamah, T. S., & Laliyo, L. A. R. (2019). Study on the Stability of Trivalent Cations Doped Zirconia through Atomistic Modeling. *Jurnal Kimia Sains Dan Aplikasi*, *22*(4), 129–135. https://doi.org/10.14710/jksa.22.4.129-135

Mczka, M., Paraguassu, W., Macalik, L., Freire, P. T. C., Hanuza, J., & Mendes Filho, J. (2011). A Raman scattering study of pressure-induced phase transitions in nanocrystalline Bi2MoO6. *Journal of Physics: Condensed Matter*, *23*(4), 45401.

Miura, K. (2002). Electronic properties of ferroelectric SrBi2Ta2O 9, SrBi2Nb2O9, and PbBi 2Nb2O9 with optimized structures. *Applied Physics Letters*. https://doi.org/10.1063/1.1474607

Phillpot, S. R., Sinnott, S. B., & Asthagiri, A. (2007). Atomic-level simulation of ferroelectricity in oxides: Current status and opportunities. *Annu. Rev. Mater. Res.*, *37*, 239–270.

Prakash, P., Garg, A., Roy, M. K., & Verma, H. C. (2007). Novel low-temperature synthesis of ferroelectric neodymium-doped bismuth titanate nanoparticles. *Journal of the American Ceramic Society*. https://doi.org/10.1111/j.1551-2916.2007.01539.x

Rosyidah, A., Onggo, D., Khairurrijal, & Ismunandar. (2008). Atomic simulations of

Aurivillius oxides: Bi3TiNbO9, Bi4Ti3O12, BaBi4Ti4O 15 and Ba2Bi4Ti5O18 doped with Pb, Al, Ga, In, Ta. *Journal of the Chinese Chemical Society*. https://doi.org/10.1002/jccs.200800018

Sadapu, S. (2015). Pengaruh Subtitusi Bi secara Parsial oleh Dopan (A= Ba, Ca, Sr dan Pb) dalam Lapisan [Bi2O2] 2+ pada Oksida Aurivillius ABi4Ti4O15. *Skripsi*, *1*(441410014).

Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*. https://doi.org/10.1107/S0567739476001551

Shimakawa, Y., Kubo, Y., Tauchi, Y., Kamiyama, T., Asano, H., & Izumi, F. (2000). Structural distortion and ferroelectric properties of SrBi2(Ta1-xNbx)2O9. *Applied Physics Letters*. https://doi.org/10.1063/1.1319509

Snedden, A., Lightfoot, P., Dinges, T., & Islam, M. S. (2004). Defect and dopant properties of the Aurivillius phase Bi4Ti3O12. *Journal of Solid State Chemistry*, *177*(10), 3660–3665.

Wendari, T. P., Arief, S., Mufti, N., Suendo, V., Prasetyo, A., Ismunandar, Baas, J., Blake, G. R., & Zulhadjri. (2019). Synthesis, structural analysis and dielectric properties of the double-layer Aurivillius compound Pb1-2xBi1.5+2xLa0.5Nb2-xMnxO9. *Ceramics International*, *45*(44), 17276–17282. https://doi.org/10.1016/j.ceramint.2019.05.285

Xiaojing, Y., Shihua, D., & Xiobing, L. (2016). The dielectric relaxor behaviour of BaTiO3 based ceramics doped with Bi and Mn. *Ferroelectrics*, *499*(1), 115–122.

Yang, X., Liu, X., & Ding, S. (2018). The defect and dielectric properties of Nb and Mn co-doping BaTiO3 ceramics. *Ferroelectrics*, *533*(1), 132–138.

akram_lakil0 0

MOLEKUL
Print ISSN: 1907-9761 e-ISSN:2503-0310

ANNOUNCEMENTS CURRENT ARCHIVES ABOUT

Search

HOME / ARCHIVES / VOL 17 NO 2 (2022) / Articles

Atomistic Simulation of La and Mn-Doped PbBi2Nb2O9 Aurivillius Phase

Atomistic Simulation of La and Mn-Doped PbBi2Nb2O9

Akram La Kilo
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Gorontalo
http://orcid.org/0000-0002-4885-1838

Ramona Nintias R. Abas
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Gorontalo

Alberto Costanzo
Dipartimento di Scienza dei Materiali e' Ingegneria Chimica, Politecnico di Torino

Daniele Mazza
Dipartimento di Scienza dei Materiali e' Ingegneria Chimica, Politecnico di Torino

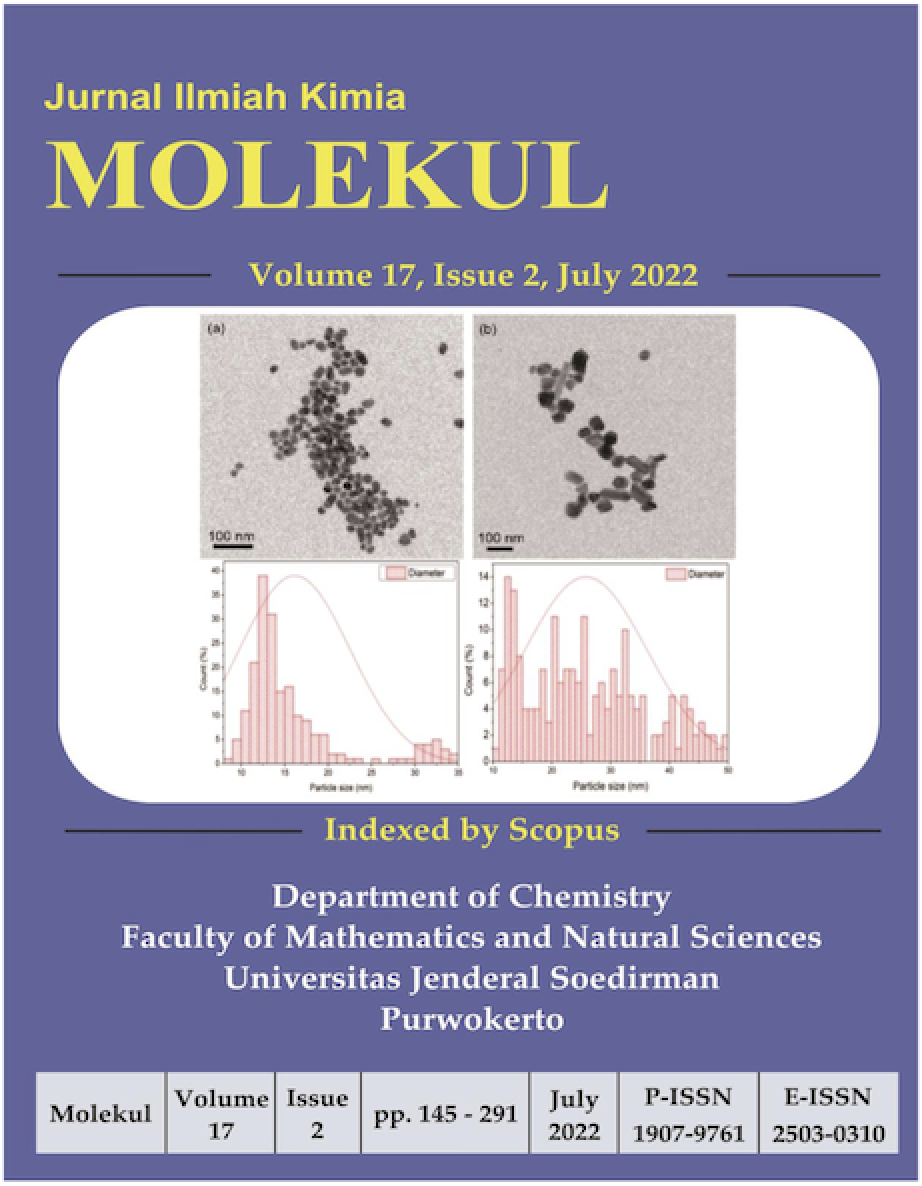
Deasy N Botutihe
Department of Educational Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Gorontalo

Jafar La Kilo
Department of Educational Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Gorontalo

DOI: https://doi.org/10.20884/1.jm.2022.17.2.6346

ABSTRACT

This study aims to determine the effect of Mn^{3+} and La^{3+} dopants on the structure of $PbBi_2Nb_2O_9$ (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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_{x}O_9$ ($x = 0$, 0.1, 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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_{x}O_9$ 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.



Jurnal Ilmiah Kimia

MOLEKUL

Volume 17, Issue 2, July 2022

Indexed by Scopus

Department of Chemistry
Faculty of Mathematics and Natural Sciences
Universitas Jenderal Soedirman
Purwokerto

Molekul	Volume 17	Issue 2	pp. 145 - 291	July 2022	P-ISSN 1907-9761	E-ISSN 2503-0310

PDF

PUBLISHED

2022-07-21

HOW TO CITE

LA KILO, Akram et al. Atomistic Simulation of La and Mn-Doped PbBi2Nb2O9 Aurivillius Phase. **Molekul**, [S.l.], v. 17, n. 2, p. 245-251, july 2022. ISSN 2503-0310. Available at: <http://jos.unsoed.ac.id/index.php/jm/article/view/6346>. Date accessed: 04 mar. 2023. doi: https://doi.org/10.20884/1.jm.2022.17.2.6346.

CITATION FORMATS

- ABNT
- APA
- BibTeX
- CBE
- EndNote - EndNote format (Macintosh & Windows)
- MLA
- ProCite - RIS format (Macintosh & Windows)
- RefWorks
- Reference Manager - RIS format (Windows only)
- Turabian

ISSUE

Vol 17 No 2 (2022)

SECTION

Articles

Authors agree with the statements below:

1. Authors automatically transfer the copyright to the MOLEKUL journal and grant the journal right of first publication with the work simultaneously licensed under a Creative Commons Attribution 4.0 International License (CC BY 4.0).
2. Authors are able to enter into separate permission for the non-exclusive distribution of the journal's published version of the work (e.g., post it to an institutional repository or publish it in a book), with an acknowledgment of its initial publication in this journal.

MAKE A SUBMISSION

FOCUS AND SCOPE

GUIDE FOR AUTHORS ▼

VIEW ARTICLES ▼

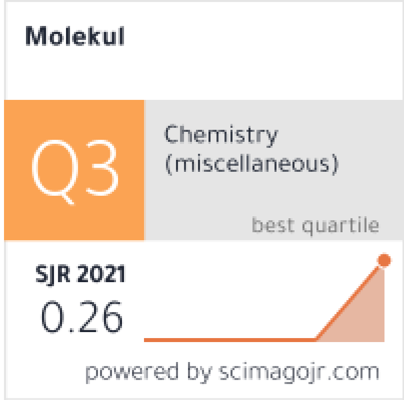
EDITORIAL BOARD

PUBLICATION ETHICS

PEER REVIEW PROCESS

PLAGIARISM POLICY

CONTACT



Molekul

Q3

Chemistry (miscellaneous)

best quartile

SJR 2021

0.26

powered by scimagojr.com

Indexing and Abstracting:

Scopus®

INDEX COPERNICUS INTERNATIONAL

sinta Science and Technology Index

DOAJ DIRECTORY OF OPEN ACCESS JOURNALS

GOOGLE ANALYTICS

Google Analytics

Matomo

Molekul

Jurnal Ilmiah Kimia
Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Universitas Jenderal Soedirman, Purwokerto, Indonesia

MOLEKUL
eISSN: 2503-0310
Articles
https://doi.org/10.20884/1.jm.2022.17.2.6346

Atomistic Simulation of La and Mn-Doped $PbBi_2Nb_2O_9$ Aurivillius Phase

Akram La Kilo[1,2]*, Ramona Nintias R. Abas[1], Alberto Costanzo[3], Daniele Mazza[3],
Deasy N. Botutihe[1,2], Jafar La Kilo [1,2]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bone Bolango Gorontalo, 96554, Indonesia
[2]Department of Educational Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Gorontalo, Jl. Habibie, Desa Moutong, Kec. Tilongkabila, Bonebolango Gorontalo, 96554, Indonesia
[3]Dipartimento 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

Received November 09, 2020; **Accepted** March 15, 2022; **Available online** July 20, 2022

ABSTRACT. This study aims to determine the effect of Mn^{3+} and La^{3+} dopants on the structure of $PbBi_2Nb_2O_9$ (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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ ($x = 0$, 0.1, 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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ 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 $PbBi_2Nb_2O_9$

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 $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ (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 $PbBi_2Nb_2O_9$ (PBN) because it has ferroelectric properties. $PbBi_2Nb_2O_9$ has orthorhombic symmetry, *A*2₁*am* group space with $a = b = 5{,}496$, and $c = 25.55$ Å, 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 $PbBi_2Nb_2O_9$ 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, 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, and 0.3). Therefore, this research look for completion to explain these two things by means of atomistic simulation of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ (x = 0.0, 0.1, 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 $PbBi_2Nb_2O_9$ (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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ (x = 0.0, 0.1, 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):

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

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):

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

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):

$$\alpha_i = \sum \frac{(Yi\ e)^2}{k_i^s} \qquad (2)$$

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 $PbBi_2Nb_2O_9$ can be predicted by calculating the Goldschmidt perovskite tolerance formulated:

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

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

$PbBi_2Nb_2O_9$ is a two-layer Aurivillius consisting of $(Bi_2O_2)^{2+}$ dan $(Pb_{n-1}Nb_nO_{3n+1})^{2-}$ 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 $PbBi_2Nb_2O_9$ 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 $PbBi_2Nb_2O_9$ 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 egreement to the two layer Aurivillius of Bi_3TiNbO_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).

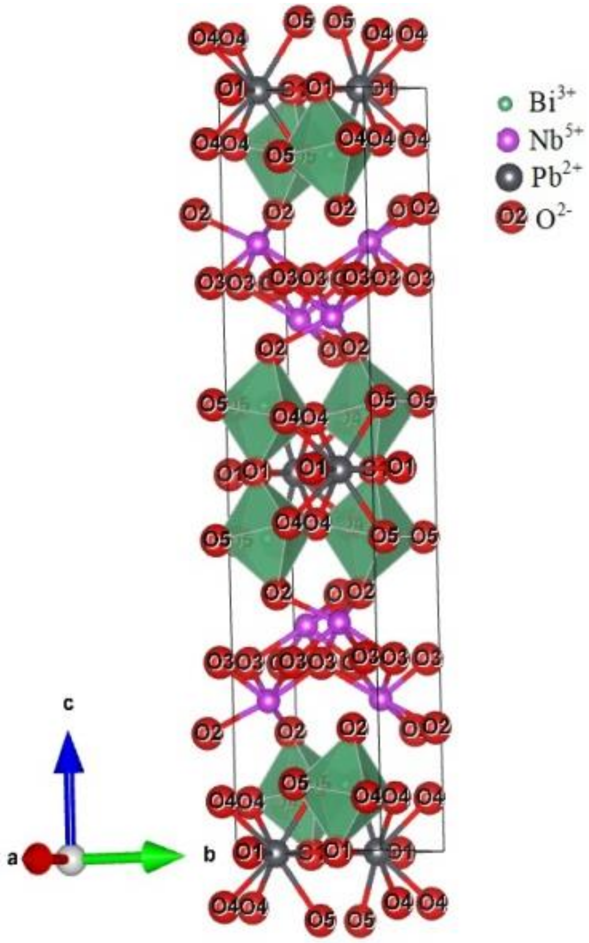


Figure 1. Crystal Structure of $PbBi_2Nb_2O_9$ (Wendari et al., 2019)

Table 1. Parameter cell of calculated and experimental $PbBi_2Nb_2O_9$

Parameter	Calculated	Exp.(Miura, 2002)	$\Delta_{(exp-calc)}$ (%)
c (Å)	5.4587	5.4960	0.68
b (Å)	5.3965	5.4960	1.81
c (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 $PbBi_2Nb_2O_9$ 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. Aurivllius 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 $PbBi_2Nb_2O_9$ doping with La^{3+} and Mn^{3+}.

In this study, La^{3+} dopant can occupy Bi^{3+} of $(Bi_2O_2)^{2+}$ 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 $PbBi_{1.5}La_{0.5}Nb_2O_9$ ($x = 0.0$) where all La^{3+} occupies a layer of $(Bi_2O_2)^{2+}$ with an occupancy of 25% of 1 Bi occupancy. PBNLM-Bi-0.1 is $Pb_{0.8}Bi_{1.7}La_{0.5}Nb_{1.9}Mn_{0.1}O_9$, where $x = 0.1$, La^{3+} occupies 0.25% of Bi site in the $(Bi_2O_2)^{2+}$ 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 $Pb_{0.4}Bi_{2.1}La_{0.5}Nb_{1.7}Mn_{0.3}O_9$ ($x = 0.3$) where La^{3+} occupies 0.25% of the site of Bi^{3+} in the $(Bi_2O_2)^{2+}$ 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 $Pb_{0.8}La_{0.7}Bi_{1.5}Nb_{1.9}Mn_{0.1}O_9$ ($x = 0.1$), where La^{3+} occupies 25% of the Bi^{3+} site in the $(Bi_2O_2)^{2+}$ layer and 20% in Pb^{2+}; Mn 5% occupies the site of Nb^{5+} in the perovskite octahedral layer. PBNLM-A-0.3 is $Pb_{0.4}La_{1.1}Bi_{1.5}Nb_{1.7}Mn_{0.3}O_9$, where $x = 0.3$, La^{3+} occupies 0.25% of the Bi^{3+} site in the $(Bi_2O_2)^{2+}$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:

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

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 $Pb_{0.8}Bi_{1.7}La_{0.5}Nb_{1.9}Mn_{0.1}O_9$ and $Pb_{0.4}Bi_{2.1}La_{0.5}Nb_{1.7}Mn_{0.3}O_9$ as they claim (Wendari et al., 2019).

Table 2. Perovskite tolerance factor of La^{3+} and Mn^{3+}-doped $PbBi_2Nb_2O_9$ aurivillius phase

Dopant composition (*x*)	Aurivillius	*t*	*t* (Wendari et al., 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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ 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 $(Bi_2O_2)^{2+}$.

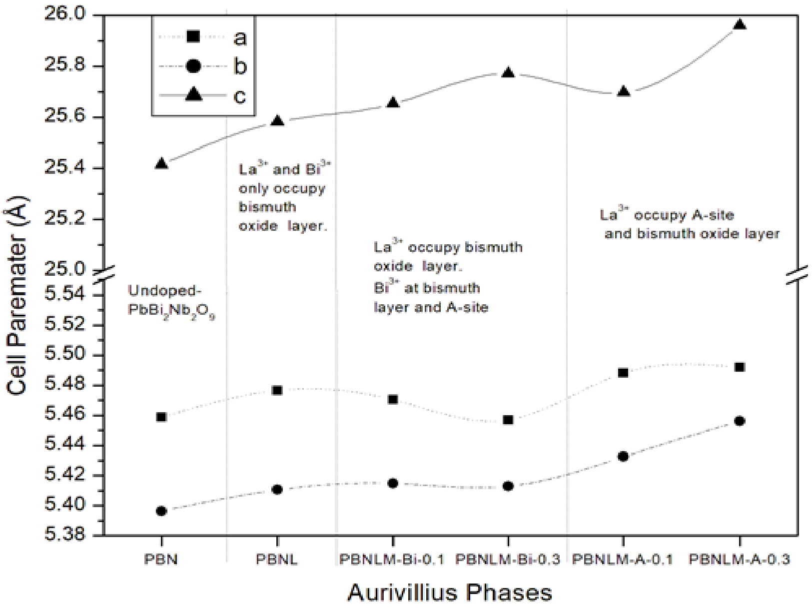


Figure 2. Lattice parameter of La^{3+} and Mn^{3+}-doped $PbBi_2Nb_2O_9$ Aurivillius Phase

Table 3. Interatomic potential of $PbBi_2Nb_2O_9$ and $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$

	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 $Bi^{3+}>Nb^{5+}>Pb^{2+}$. 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 $SrBi_2(Ta_{1-x}Nb_x)_2O_9$ 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 Bi...O>Pb...O>Nb...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 $ABi_4Ti_4O_{15}$ (A = Ba, Ca, Sr, 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).

$PbBi_2Nb_2O_9$ lattice energy is much smaller than the Bi_3TiNbO_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 Aurivillus which in theory will have more energy than the Aurivilius lattice energy with the octahedral layer above it. But these results are contrary to what is expected. In fact, $PbBi_2Nb_2O_9$ has a lower lattice energy compared to the four-layer Aurivillius lattice energy of $BaBi_4Ti_4O_{15}$ (-770.64590 eV) and $Ba_2Bi_4Ti_5O_{18}$ (-927.2781 eV), which means

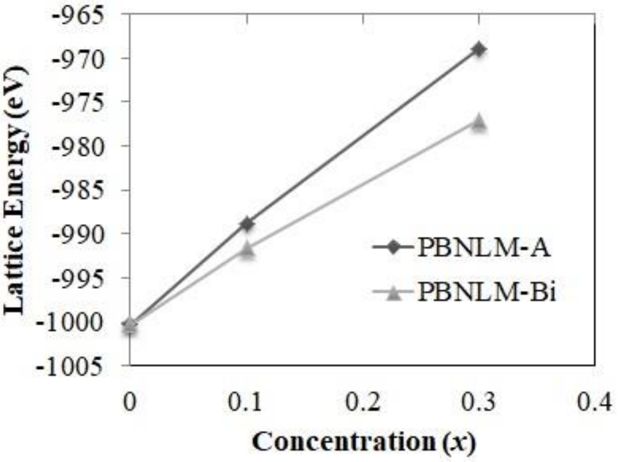


Figure 3. Lattice Energy of Mn^{3+} and La^{3+}-doped $PbBi_2Nb_2O_9$

that the $PbBi_2Nb_2O_9$ 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 $PbBi_2Nb_2O_9$ 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 $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ 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 Aurivellius 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, $PbBi_2Nb_2O_9$. Bi^{3+} which partially substituted Pb^{2+} in the perovskite layer causes the structure of $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$ (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 $PbBi_2Nb_2O_9$phase being less stable. PBNLM-Bi is predicted more easily synthesized compared to PBNLM-A.

ACKNOWLEDMENTS

The authors thank to Ms. Triwahyuni Umamah for technical assistance. The research was financed by Universitas Negeri Gorontalo with grant number: B/142/UN47.D1/PT.01.03/202 of PNBP Basic research.

REFERENCES

Aurivillius, B. (1949a). Mixed Bismuth Oxides with Layer lattices: I The Structure Type of CaBi2Nb2O9. *Arkiv Kemi Band I.*

Aurivillius, B. (1949b). Mixed bismuth oxides with layer lattices. II. Structure of Bi4Ti3O12. *Arkiv for Kemi*.

Born, M., & Mayer, J. E. (1932). Zur Gittertheorie der Ionenkristalle. *Zeitschrift Für Physik*. https://doi.org/10.1007/BF01340511

Dutra, J. D. L., Bispo, T. D., de Freitas, S. M., & dos S. Rezende, M. V. (2021). ParamGULP: An efficient Python code for obtaining interatomic potential parameters for General Utility Lattice Program. *Computer Physics Communications*, *265*, 107996. https://doi.org/https://doi.org/10.1016/j.cpc.2021.107996

Gale, J. D. (1997). GULP: A computer program for the symmetry-adapted simulation of solids. *Journal of the Chemical Society - Faraday Transactions*. https://doi.org/10.1039/a606455h

Gale, J. D., & Rohl, A. L. (2003). The General Utility Lattice Program (GULP). *Molecular Simulation*. https://doi.org/10.1080/0892702031000104887

Goldschmidt, V. M. (1926). Die gesetze der krystallochemie. *Naturwissenschaften*, *14*(21), 477–485.

Islam, M. S., Lazure, S., Vannier, R., Nowogrocki, G., & Mairesse, G. (1998). Structural and computational studies of Bi 2 WO 6 based oxygen ion conductors. *Journal of Materials Chemistry*, *8*(3), 655–660.

Ismunandar, Kennedy, B. J., Gunawan, & Marsongkohadi. (1996). Structure of ABi2Nb2O9 (A = Sr, Ba): Refinement of powder neutron diffraction data. *Journal of Solid State Chemistry*, *126*(1),135. https://doi.org/10.1006/jssc.1996.0321

Kilo, A. La, Prijamboedi, B., Martoprawiro, M. A., & Ismunandar. (2011). Modeling ionic conduction in γ-Bi 2VO 5.5. *Proceedings - International Conference on Instrumentation, Communication, Information Technology and Biomedical Engineering 2011, ICICI-BME 2011*. https://doi.org/10.1109/ICICI-BME. 2011. 6108652

Kim, H. G., Hwang, D. W., & Lee, J. S. (2004). An undoped, single-phase oxide photocatalyst working under visible light. *Journal of the American Chemical Society*, *125*(29) https://doi.org/10.1021/ja049676a

La Kilo, A., Costanzo, A., Mazza, D., Martoprawiro, M. A., Prijamboedi, B., & Ismunandar, I. (2020). Highest ionic conductivity of BIMEVOX (ME = 10% Cu, 10% Ga, 20% Ta): Computational modeling and simulation. *Indonesian Journal of Chemistry*, *20*(3), 510. https://doi.org/10.22146/ijc.42635

La Kilo, A., & Mazza, D. (2011). Pemodelan konduktivitas ion dalam struktur $Li_2Sc_3(PO_4)_3$ (Modeling ionic conductivity in $Li_2Sc_3(PO_4)_3$ structure). *Jurnal Manusia Dan Lingkungan*, *18*(3), 179–183. https://doi.org/https://doi.org/ 10.22146/jml.18439

La Kilo, A., Umamah, T. S., & Laliyo, L. A. R. (2019). Study on the Stability of Trivalent Cations Doped Zirconia through Atomistic Modeling. *Jurnal Kimia Sains Dan Aplikasi*, *22*(4), 129–135. https://doi.org/10.14710/jksa.22.4.129-135

Mczka, M., Paraguassu, W., Macalik, L., Freire, P. T. C., Hanuza, J., & Mendes Filho, J. (2011). A Raman scattering study of pressure-induced phase transitions in nanocrystalline Bi2MoO6. *Journal of Physics: Condensed Matter*, *23*(4), 45401.

Miura, K. (2002). Electronic properties of ferroelectric SrBi2Ta2O 9, SrBi2Nb2O9, and PbBi 2Nb2O9 with optimized structures. *Applied Physics Letters*, 80, 2967. https://doi.org/10.1063/ 1.1474607

Phillpot, S. R., Sinnott, S. B., & Asthagiri, A. (2007). Atomic-level simulation of ferroelectricity in oxides: Current status and opportunities. *Annu. Rev. Mater. Res.*, *37*, 239–270.

Prakash, P., Garg, A., Roy, M. K., & Verma, H. C. (2007). Novel low-temperature synthesis of ferroelectric neodymium-doped bismuth titanate nanoparticles. *Journal of the American Ceramic Society*, *90*(4). https://doi.org/ 10.1111/j.1551-2916.2007.01539.x

Rosyidah, A., Onggo, D., Khairurrijal, & Ismunandar. (2008). Atomic simulations of Aurivillius oxides: Bi3TiNbO9, $Bi_4Ti_3O_{12}$, $BaBi_4Ti_4O_{15}$ and $Ba_2Bi_4Ti_5O_{18}$ doped with Pb, Al, Ga, In, Ta. *Journal of the Chinese Chemical Society*, *55*(1) https://doi.org/10.1002/jccs.200800018

Sadapu, S. (2015). Pengaruh Subtitusi Bi secara Parsial oleh Dopan (A= Ba, Ca, Sr dan Pb) dalam Lapisan $[Bi_2O_2]^{2+}$ pada Oksida Aurivillius $ABi_4Ti_4O_{15}$. *Skripsi*, *1*(441410014).

Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*, *A32*, 751-767 https://doi.org/10.1107/S0567739476001551

Shimakawa, Y., Kubo, Y., Tauchi, Y., Kamiyama, T., Asano, H., & Izumi, F. (2000). Structural distortion and ferroelectric properties of $SrBi_2(Ta_{1-x}Nb_x)_2O_9$. *Applied Physics Letters*, *77*,2749 https://doi.org/10.1063/1.1319509

Snedden, A., Lightfoot, P., Dinges, T., & Islam, M. S. (2004). Defect and dopant properties of the Aurivillius phase $Bi_4Ti_3O_{12}$. *Journal of Solid State Chemistry*, *177*(10), 3660–3665.

Wendari, T. P., Arief, S., Mufti, N., Suendo, V., Prasetyo, A., Ismunandar, Baas, J., Blake, G. R., & Zulhadjri. (2019). Synthesis, structural analysis and dielectric properties of the double-layer Aurivillius compound $Pb_{1-2x}Bi_{1.5+2x}La_{0.5}Nb_{2-x}Mn_xO_9$. *Ceramics International*, *45*(44), 17276–17282. https://doi.org/10.1016/ j.ceramint.2019.05.285

Xiaojing, Y., Shihua, D., & Xiobing, L. (2016). The dielectric relaxor behaviour of BaTiO3 based ceramics doped with Bi and Mn. *Ferroelectrics*, *499*(1), 115–122.

Yang, X., Liu, X., & Ding, S. (2018). The defect and dielectric properties of Nb and Mn co-doping $BaTiO_3$ ceramics. *Ferroelectrics*, *533*(1), 132–138.