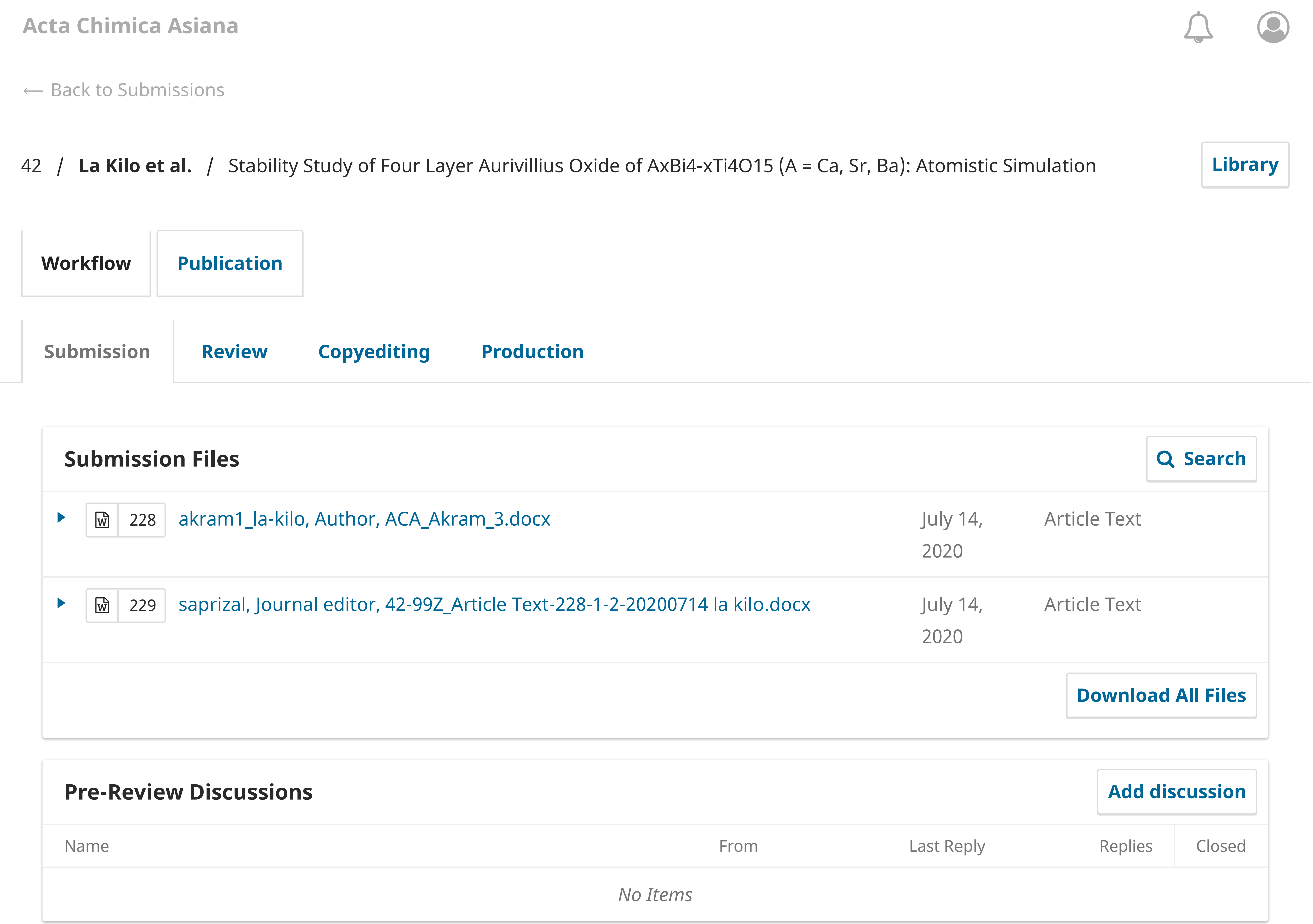


42 / **La Kilo et al.** / Stability Study of Four Layer Aurivillius Oxide of AxBi4-xTi4O15 (A = Ca, Sr, Ba): Atomistic Simulation

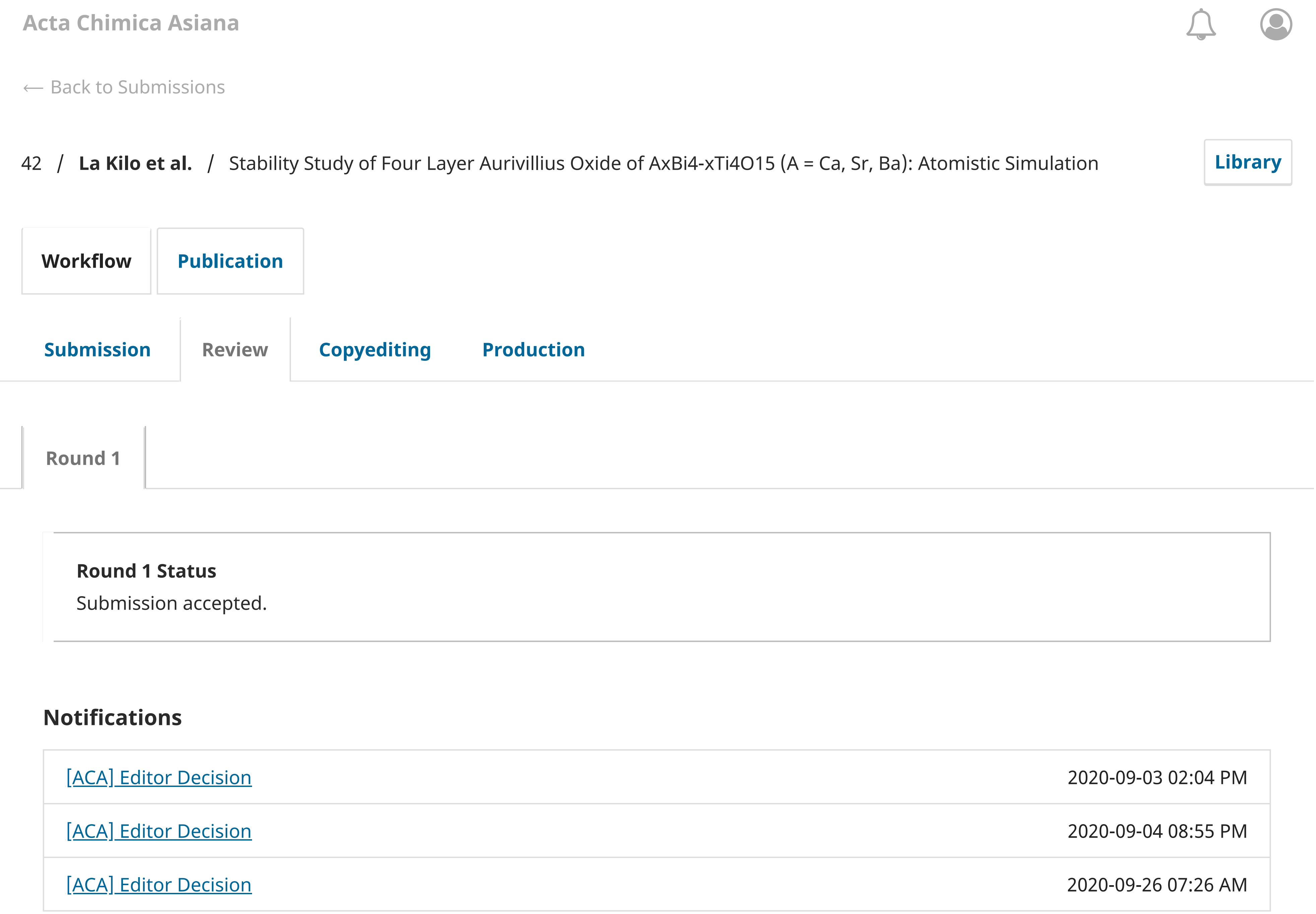
Submission Files

228	akram1_la-kilo, Author, ACA_Akram_3.docx	July 14, 2020	Article Text
229	saprizal, Journal editor, 42-99Z_Article Text-228-1-2-20200714 la kilo.docx	July 14, 2020	Article Text

Pre-Review Discussions

Name	From	Last Reply	Replies	Closed

No Items



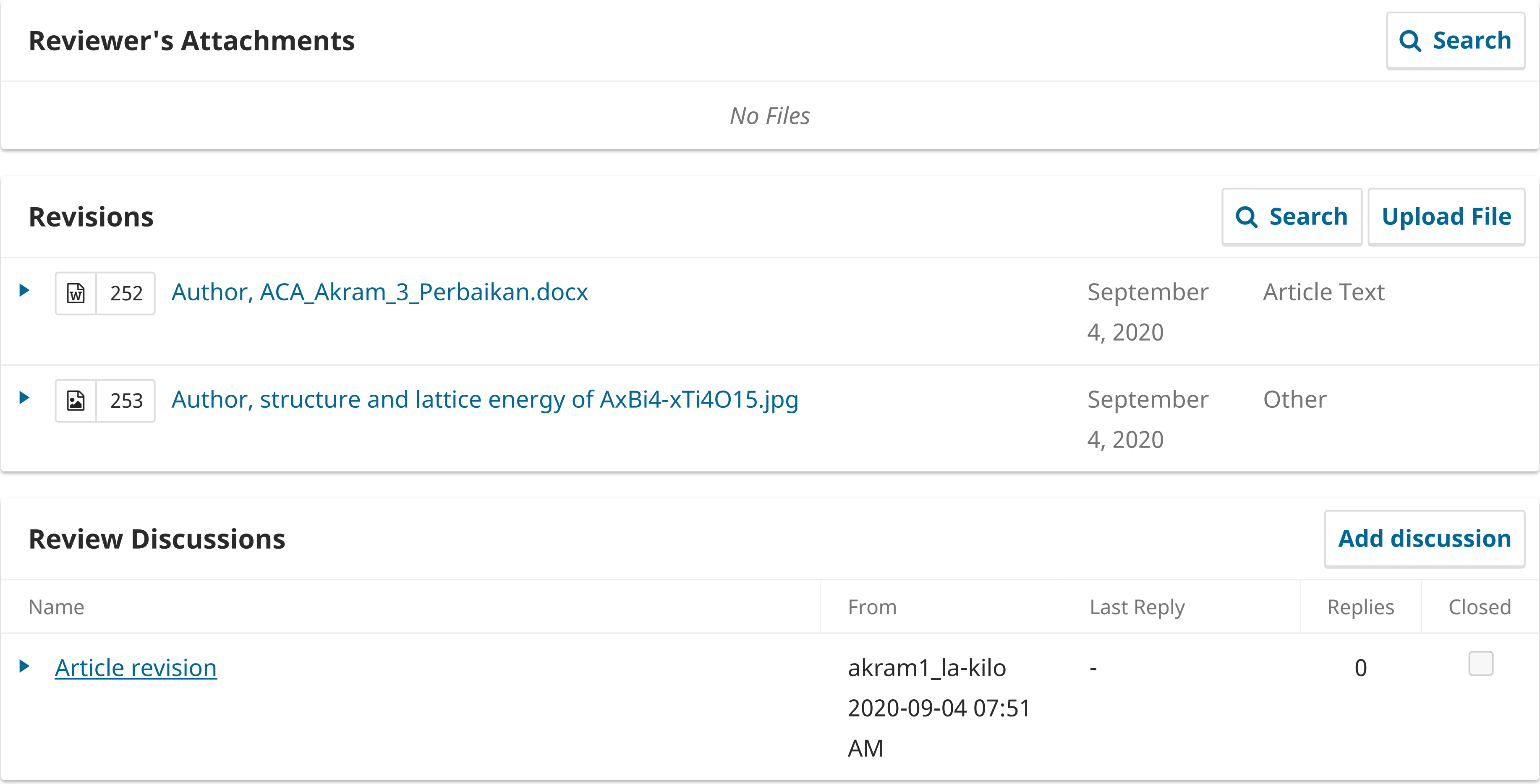
42 / **La Kilo et al.** / Stability Study of Four Layer Aurivillius Oxide of $A_xBi_{4-x}Ti_4O_{15}$ (A = Ca, Sr, Ba): Atomistic Simulation

Round 1 Status

Submission accepted.

Notifications

[ACA] Editor Decision	2020-09-03 02:04 PM
[ACA] Editor Decision	2020-09-04 08:55 PM
[ACA] Editor Decision	2020-09-26 07:26 AM



Reviewer's Attachments

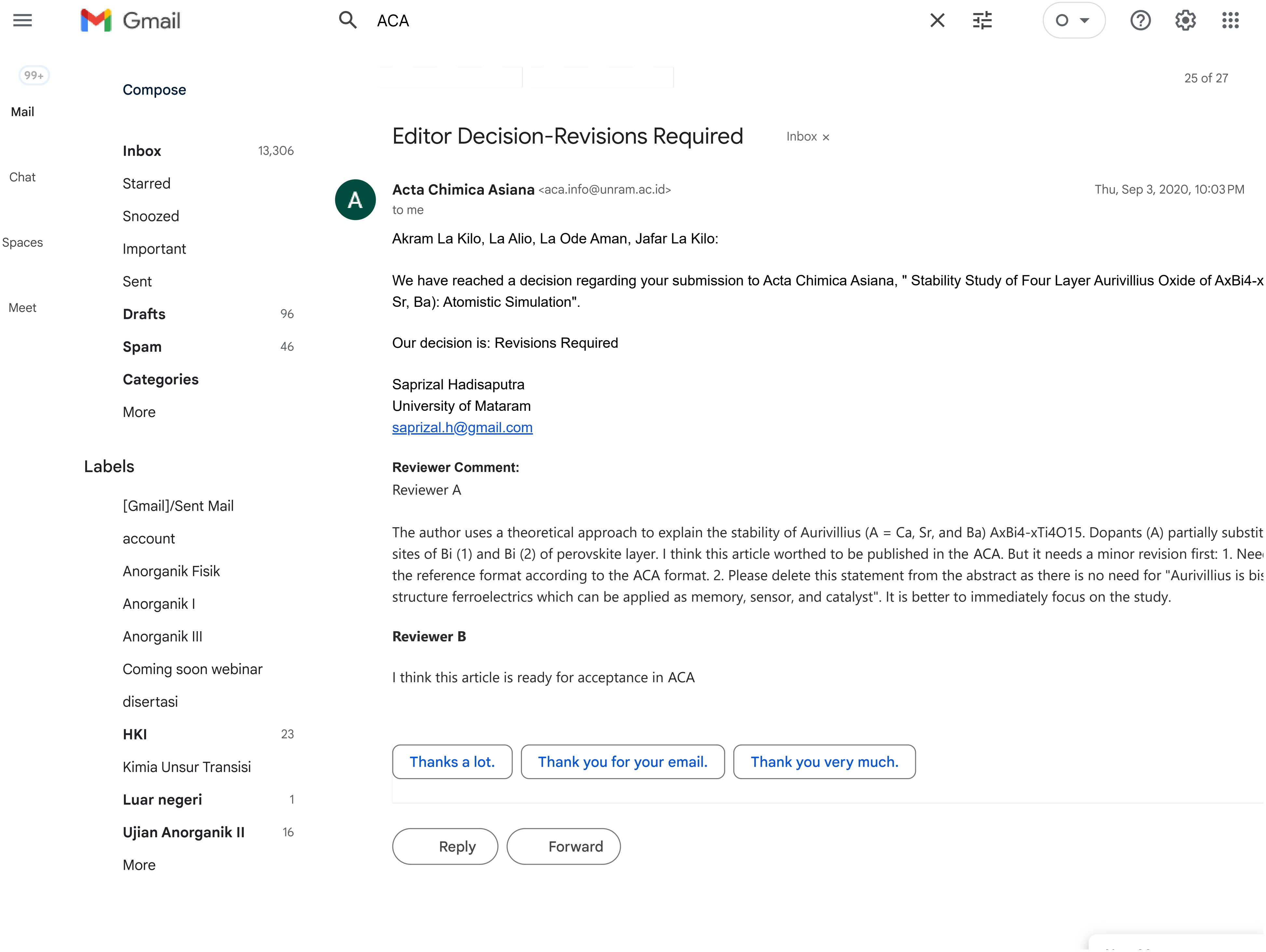
No Files

Revisions

▸	252	Author, ACA_Akram_3_Perbaikan.docx	September 4, 2020	Article Text
▸	253	Author, structure and lattice energy of AxBi4-xTi4O15.jpg	September 4, 2020	Other

Review Discussions

Name	From	Last Reply	Replies	Closed
▸ Article revision	akram1_la-kilo 2020-09-04 07:51 AM	-	0	☐



Editor Decision-Revisions Required

Acta Chimica Asiana <aca.info@unram.ac.id>
to me

Thu, Sep 3, 2020, 10:03 PM

Akram La Kilo, La Alio, La Ode Aman, Jafar La Kilo:

We have reached a decision regarding your submission to Acta Chimica Asiana, " Stability Study of Four Layer Aurivillius Oxide of AxBi4-x
Sr, Ba): Atomistic Simulation".

Our decision is: Revisions Required

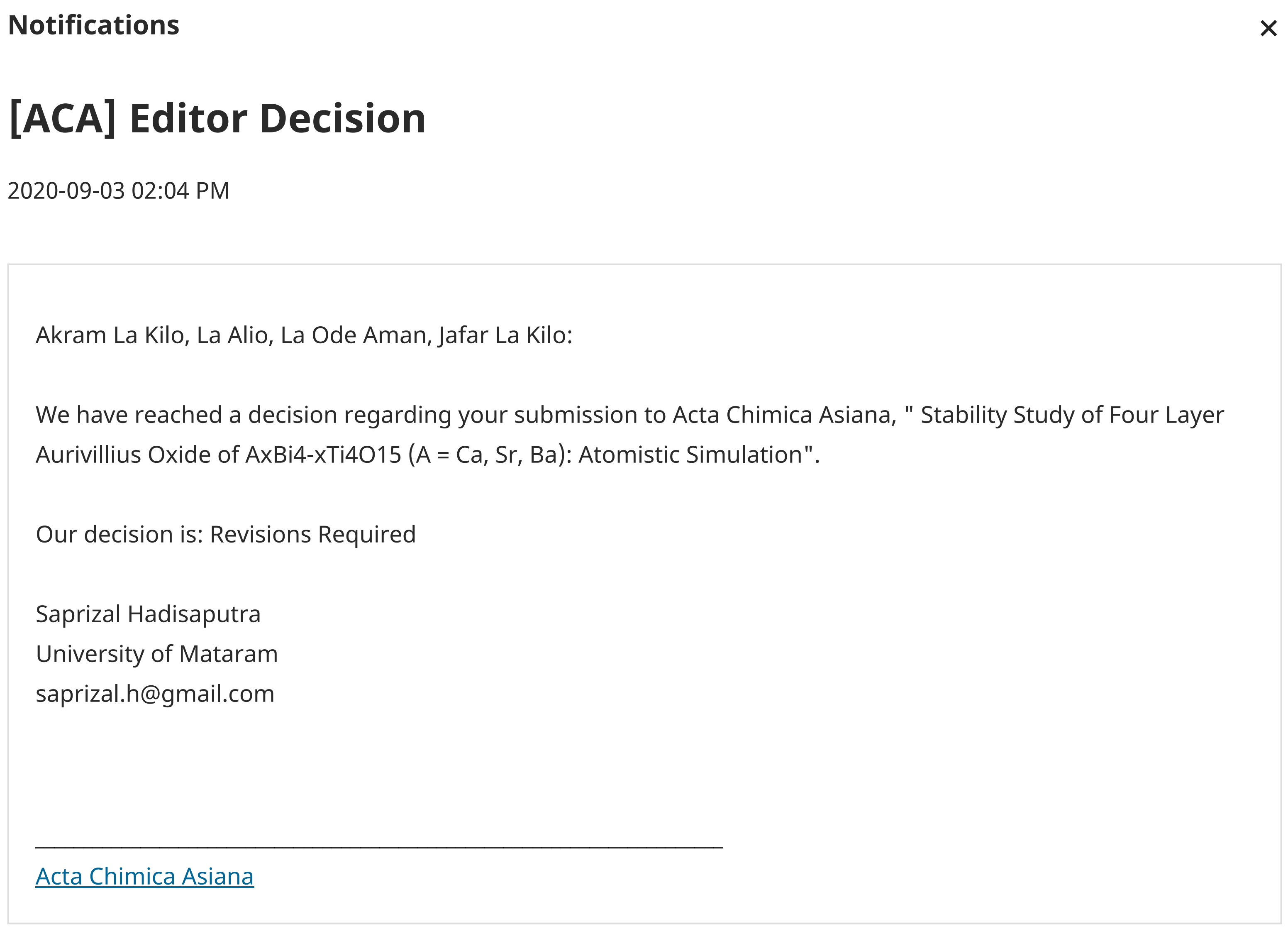
Saprizal Hadisaputra
University of Mataram
saprizal.h@gmail.com

Reviewer Comment:
Reviewer A

The author uses a theoretical approach to explain the stability of Aurivillius (A = Ca, Sr, and Ba) AxBi4-xTi4O15. Dopants (A) partially substit
sites of Bi (1) and Bi (2) of perovskite layer. I think this article worthed to be published in the ACA. But it needs a minor revision first: 1. Nee
the reference format according to the ACA format. 2. Please delete this statement from the abstract as there is no need for "Aurivillius is bi
structure ferroelectrics which can be applied as memory, sensor, and catalyst". It is better to immediately focus on the study.

Reviewer B

I think this article is ready for acceptance in ACA



[ACA] Editor Decision

2020-09-03 02:04 PM

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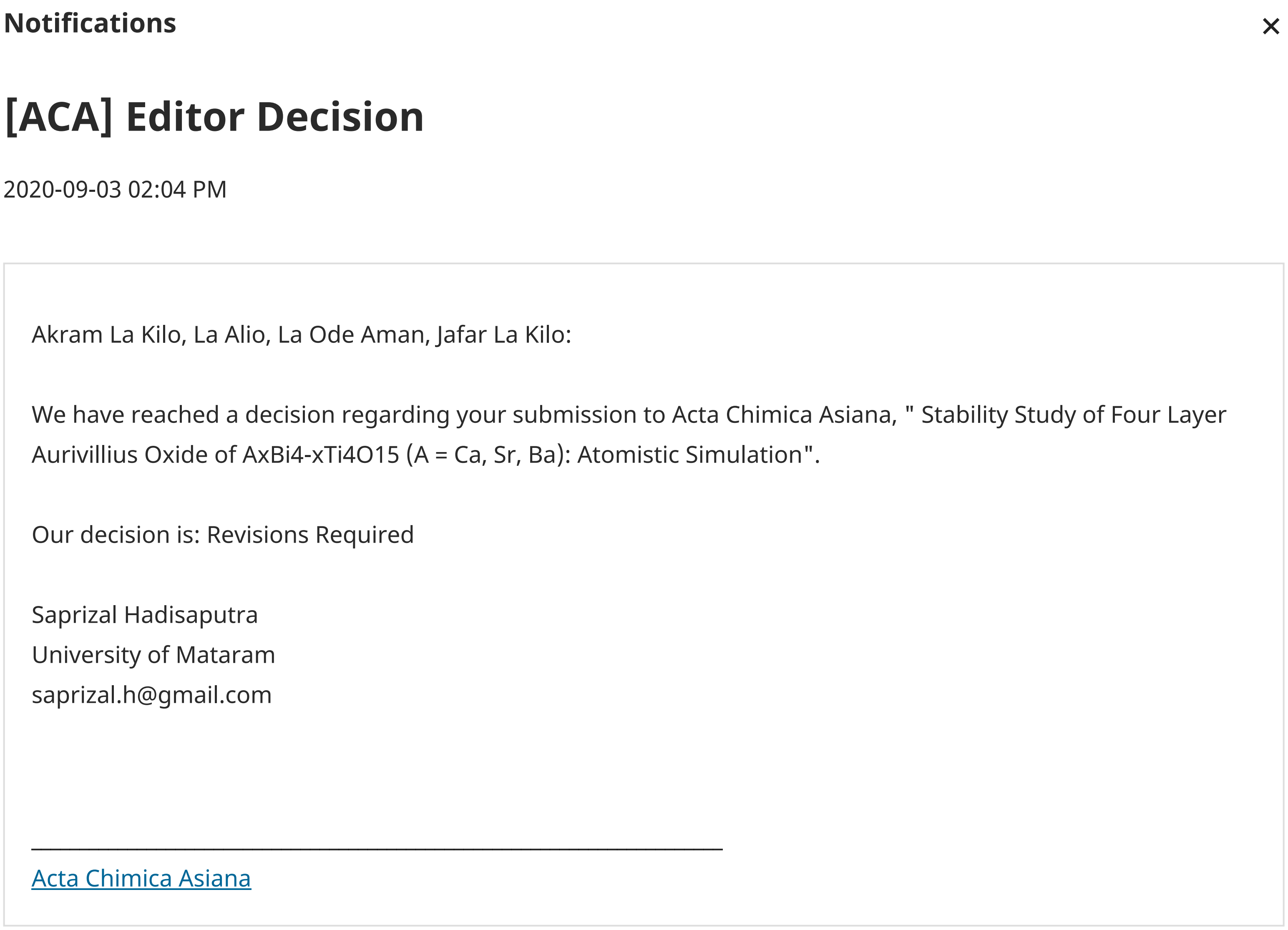

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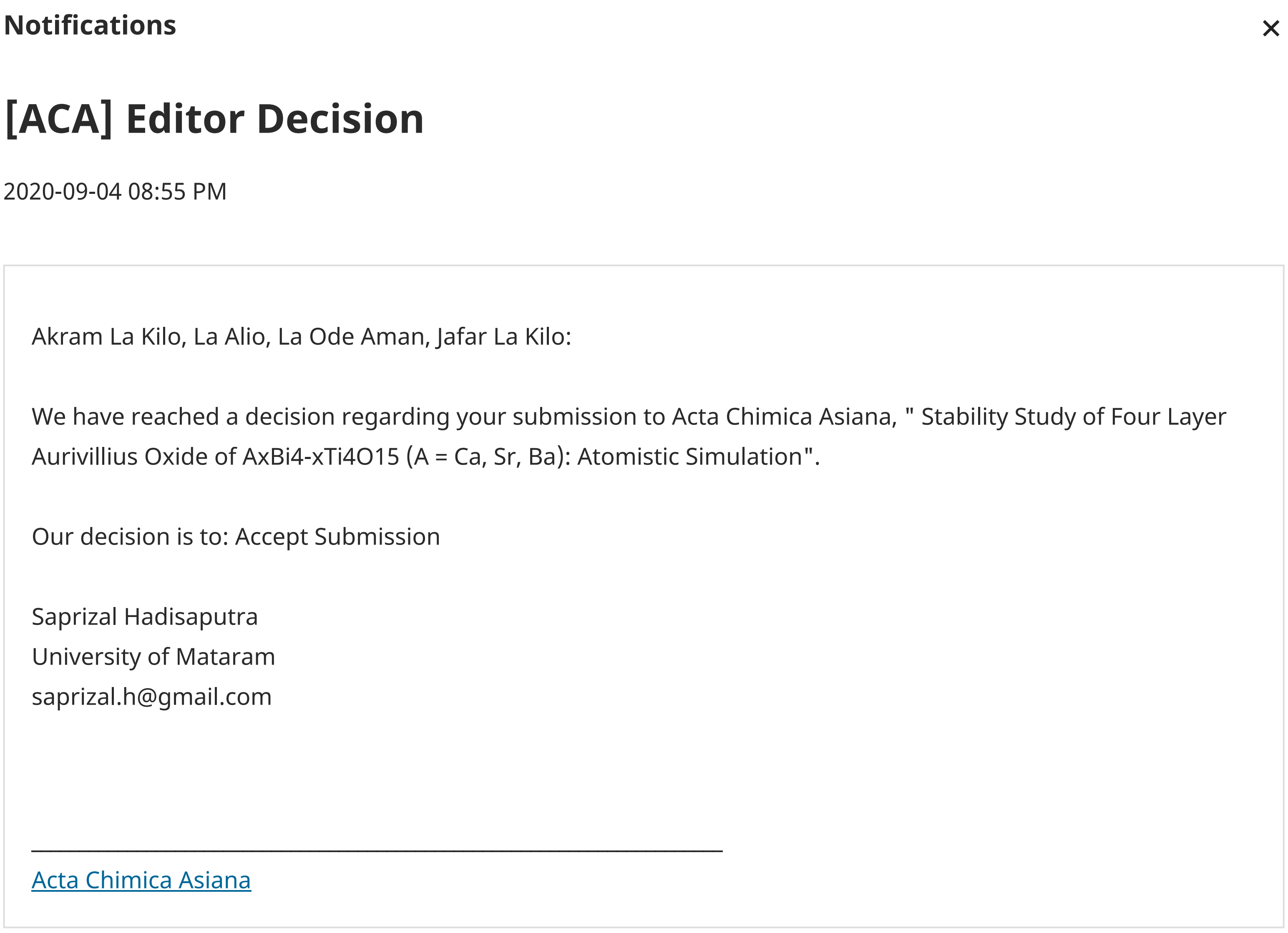

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2020-09-04 08:55 PM

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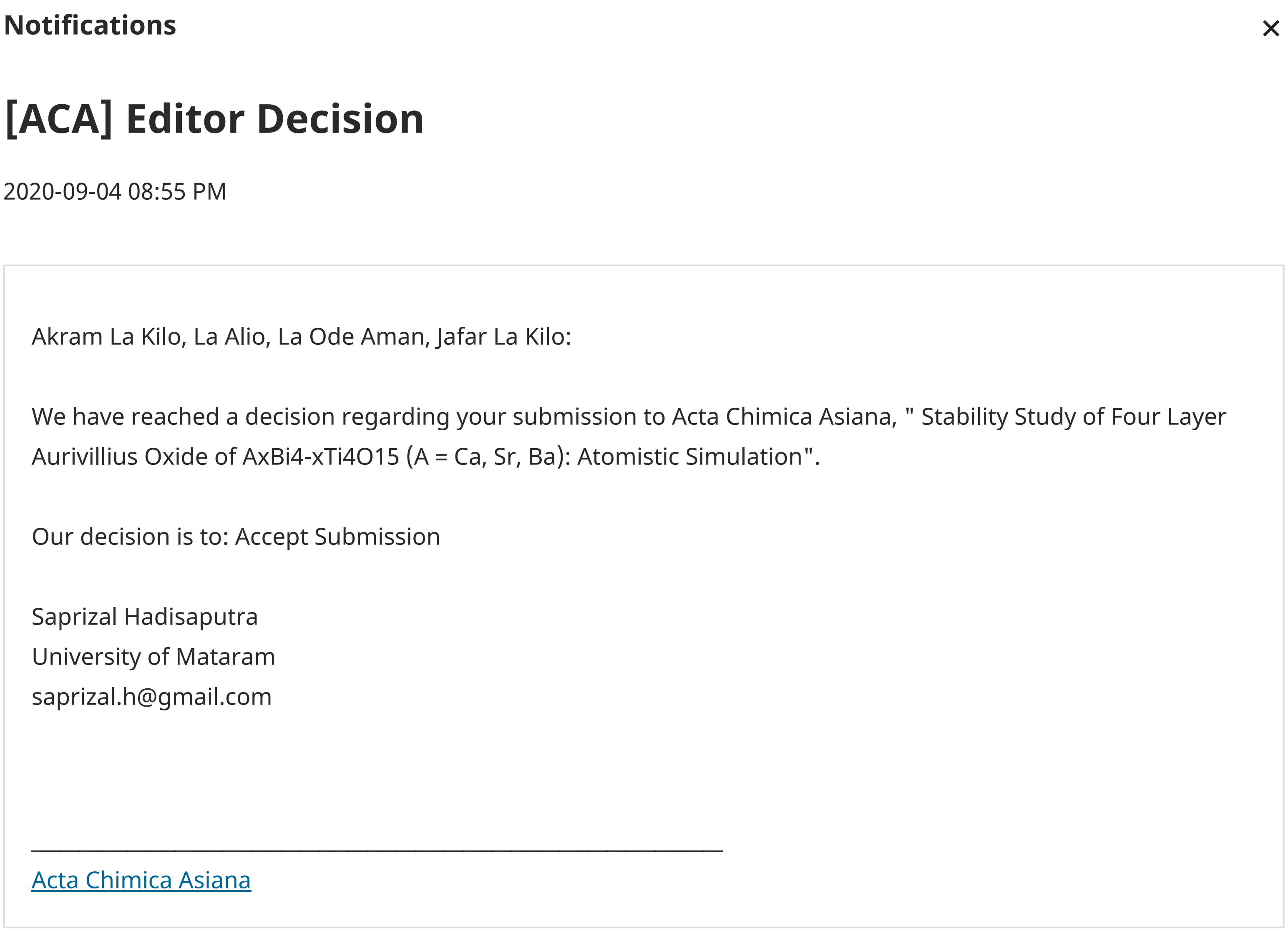

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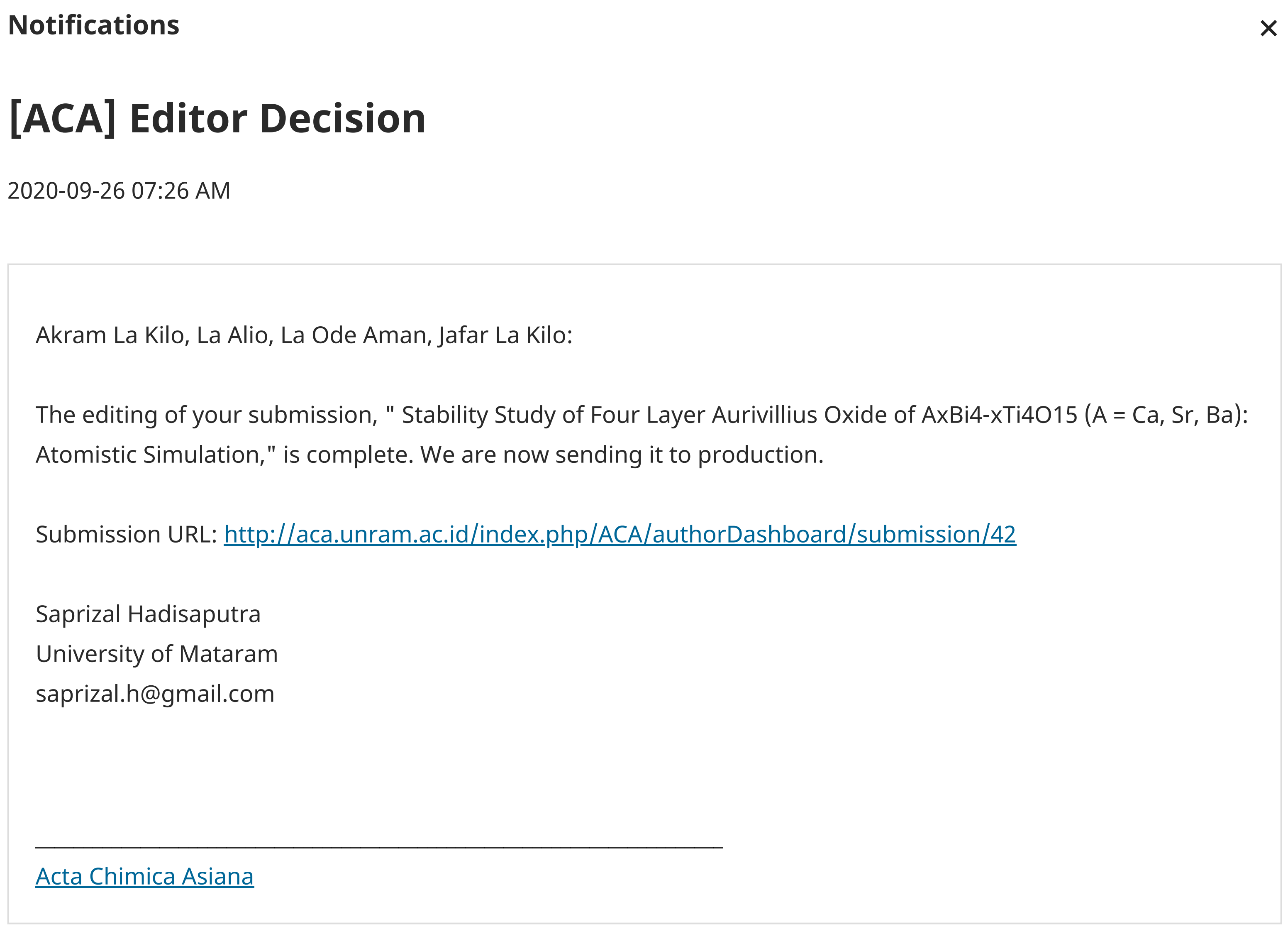

Notifications

[ACA] Editor Decision

2020-09-26 07:26 AM

Akram La Kilo, La Alio, La Ode Aman, Jafar La Kilo:

The editing of your submission, " Stability Study of Four Layer Aurivillius Oxide of AxBi4-xTi4O15 (A = Ca, Sr, Ba): Atomistic Simulation," is complete. We are now sending it to production.

Submission URL: http://aca.unram.ac.id/index.php/ACA/authorDashboard/submission/42

Saprizal Hadisaputra
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Acta Chimica Asiana

Notifications ✕

[ACA] Editor Decision

2020-09-26 07:26 AM

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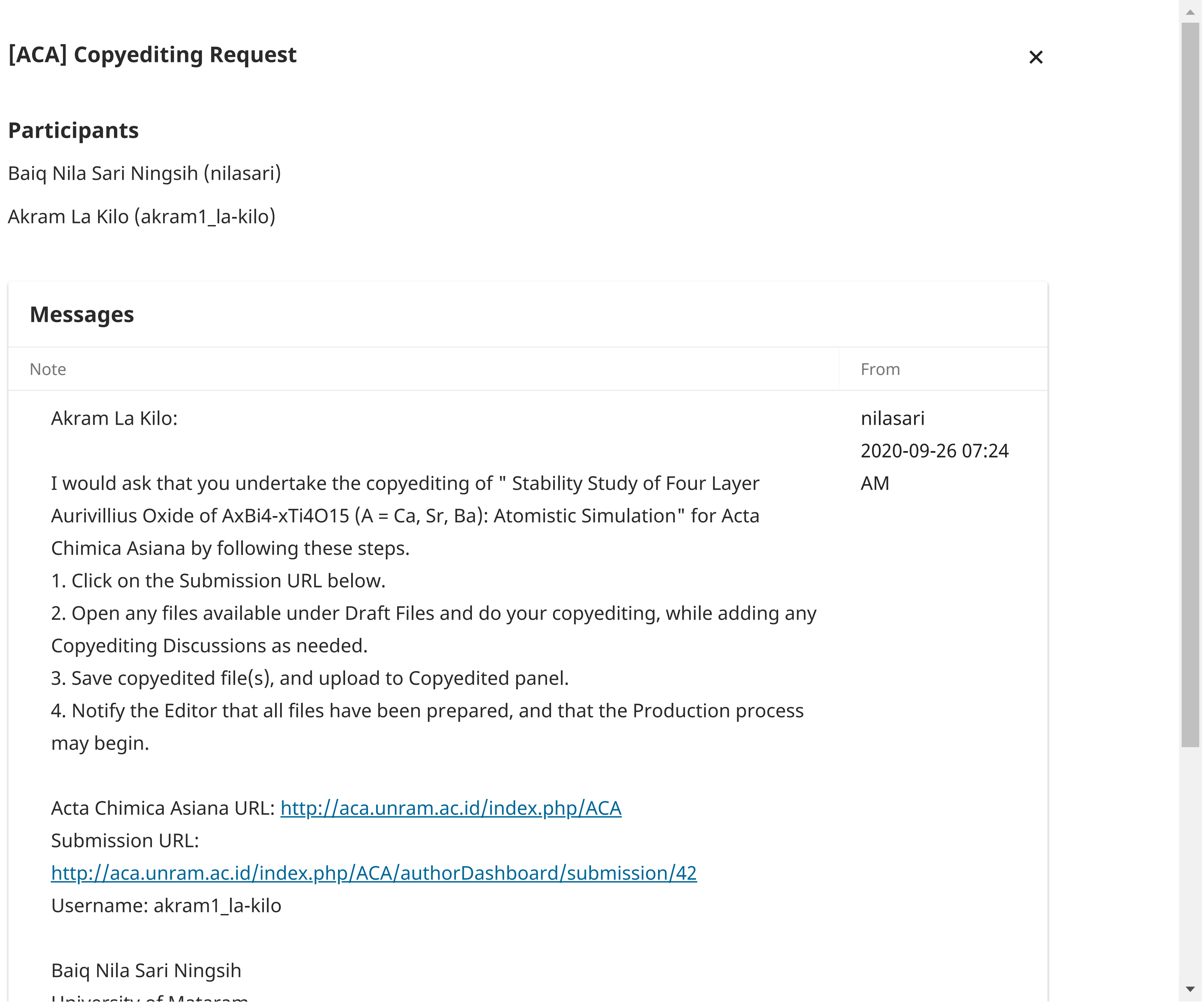


[ACA] Copyediting Request

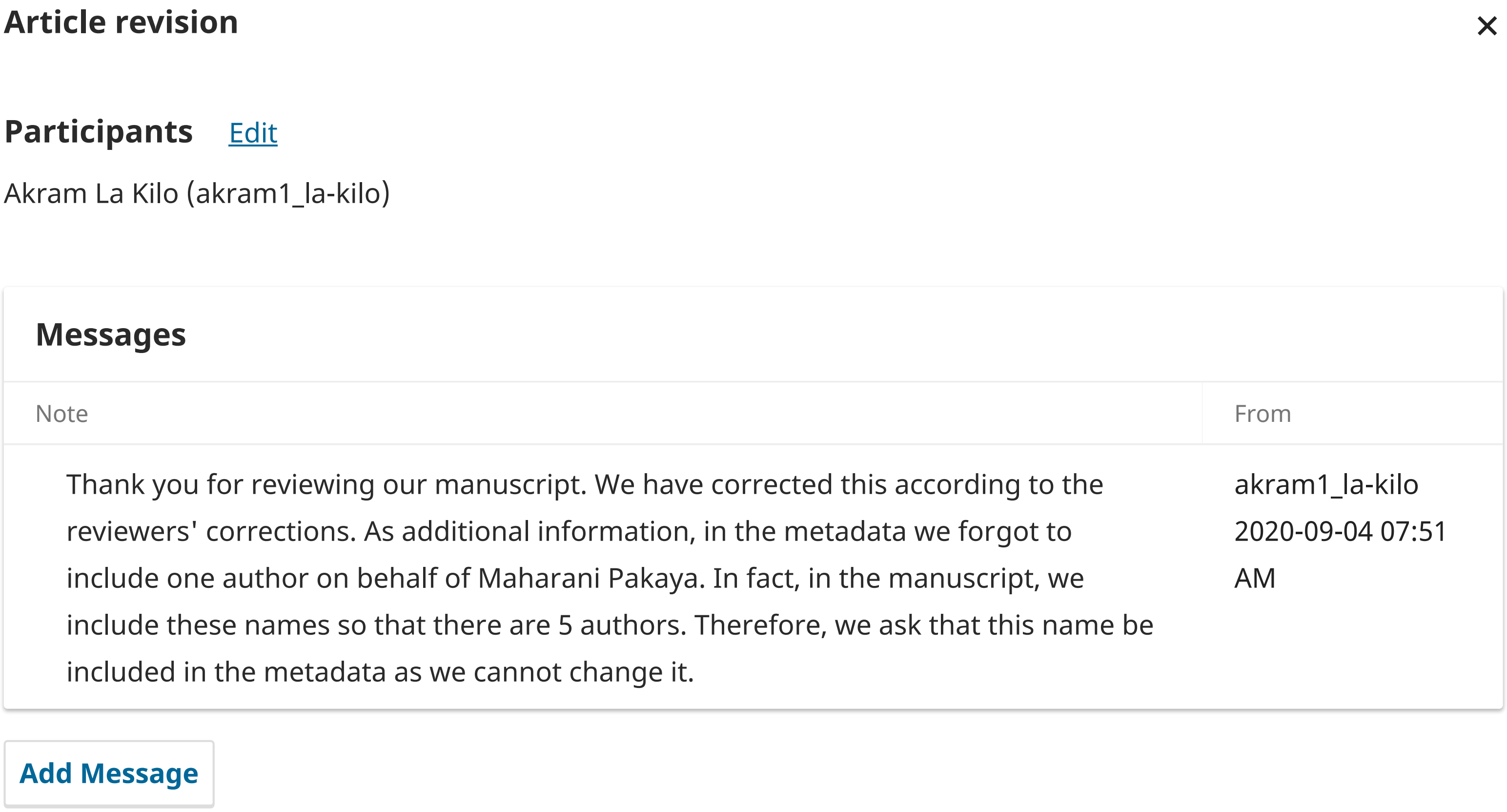
Participants

Baiq Nila Sari Ningsih (nilasari)

Akram La Kilo (akram1_la-kilo)

Messages

Note	From
Akram La Kilo: I would ask that you undertake the copyediting of " Stability Study of Four Layer Aurivillius Oxide of AxBi4-xTi4O15 (A = Ca, Sr, Ba): Atomistic Simulation" for Acta Chimica Asiana by following these steps. 1. Click on the Submission URL below. 2. Open any files available under Draft Files and do your copyediting, while adding any Copyediting Discussions as needed. 3. Save copyedited file(s), and upload to Copyedited panel. 4. Notify the Editor that all files have been prepared, and that the Production process may begin. Acta Chimica Asiana URL: http://aca.unram.ac.id/index.php/ACA Submission URL: http://aca.unram.ac.id/index.php/ACA/authorDashboard/submission/42 Username: akram1_la-kilo Baiq Nila Sari Ningsih University of Mataram	nilasari 2020-09-26 07:24 AM



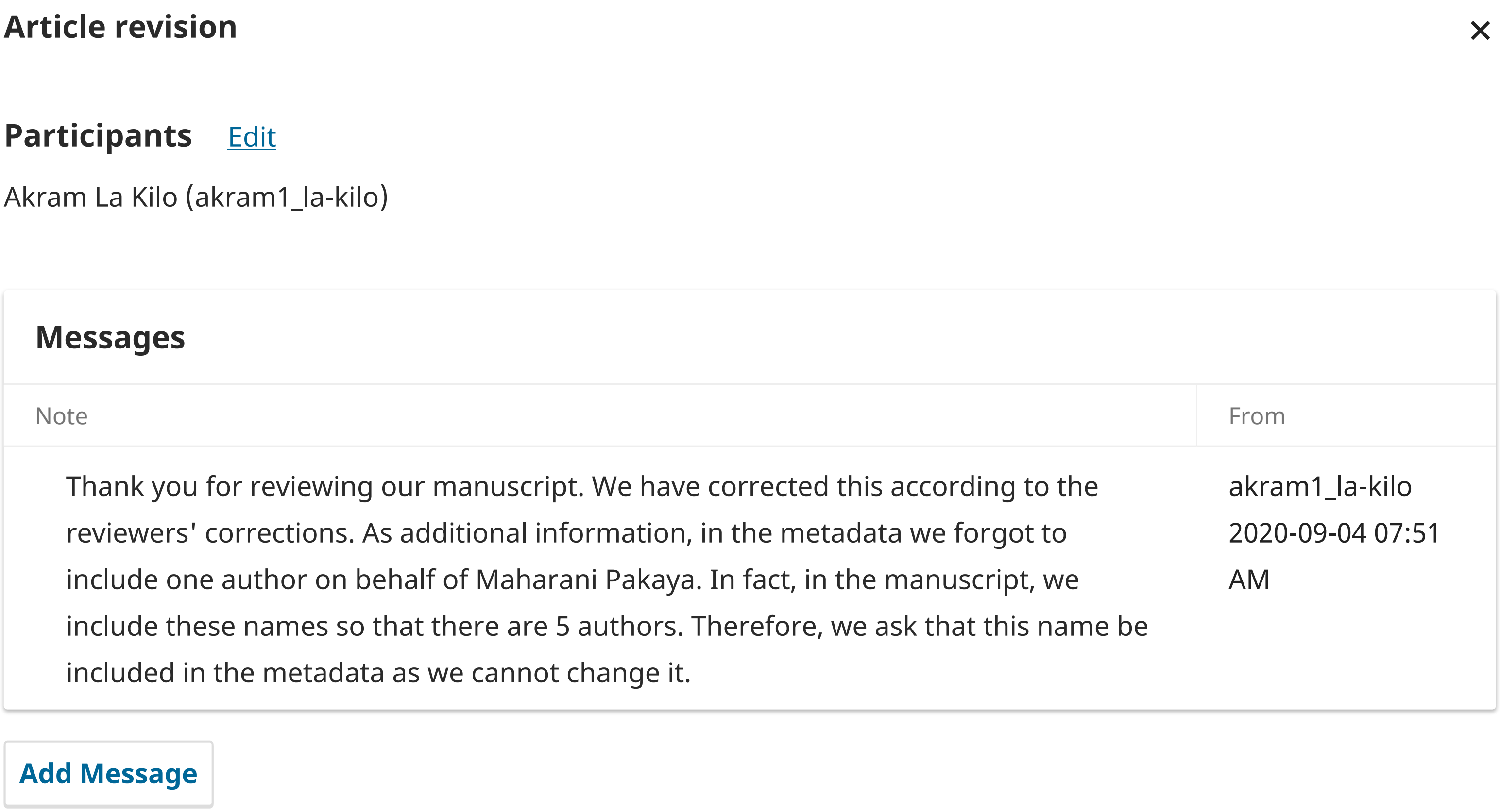
Article revision

Participants

Akram La Kilo (akram1_la-kilo)

Messages

Note	From
Thank you for reviewing our manuscript. We have corrected this according to the reviewers' corrections. As additional information, in the metadata we forgot to include one author on behalf of Maharani Pakaya. In fact, in the manuscript, we include these names so that there are 5 authors. Therefore, we ask that this name be included in the metadata as we cannot change it.	akram1_la-kilo 2020-09-04 07:51 AM



Article revision

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RESEARCH PAPER

Stability Study of Four Layer Aurivillius Oxide of $A_xBi_{4-x}Ti_4O_{15}$ (A = Ca, Sr, Ba): Atomistic Simulation

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Abstract: Aurivillius is bismuth layered structure ferroelectrics which can be applied as memory, sensor, and catalyst. This research aimed to study the stability of $A_xBi_{4-x}Ti_4O_{15}$ Aurivillius (A = Ca, Sr, and Ba). Dopants (A) partially substitute Bi at the sites of Bi(1) and Bi(2) of perovskite layer. This research method is atomistic simulation using by GULP code. Simulations were carried out by means of $A_xBi_{4-x}Ti_4O_{15}$ geometry optimization at a constant pressure, using the Buckingham potential. The results showed that the increase in the concentration of dopants substituting Bi accompanied with increase in lattice energies. The most stable Aurivillius was $Ca_xBi_{4-x}Ti_4O_{15}$ (x = 16.3%) carried out by Bi substitution at Bi(2) site, with lattice energy, -1668.227 eV. Aurivillius stability decreases by increasing size of the dopant. The maximum concentration number of A dopant substituting Bi was discussed.

Keywords: Aurivillius; Atomistic simulation; lattice energy; dopants of earth alkaline ionic; shell model

INTRODUCTION

The specific nature of Aurivillius is determined by its crystal structure [1]. The packaging of the ions in the structure determines type and possibility of Aurivillius application [2]. One of the interesting properties of Aurvillius is ferroelectric which can be applied as a storage material of Fe-RAM memory, capacitors, piezoelectric, conductor, catalyst, and as a magnetic material [3], [4]. To achieve the property, then Aurvillius doped with certain ions on bismuth oxide or perovskite layers.

Aurivillius oxide is an oxide compound with a layered structure that is arranged regularly and alternates between layers of perovskite of $[A_{n-1}B_nO_{3n+1}]^{2-}$ and $[Bi_2O_2]^{2+}$. Cation A is dodecahedral coordinated ions, which have a charge of +1, +2 or +3, such as alkali, earth alkaline, rare earth elements or mixtures. Cation B is ions with octahedral coordination which are usually transition elements with smaller sizes than cation A. While *n* is an integer which shows the octahedral number in the perovskite layer [5], [6].

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Layered oxide has structural and composition flexibility that allows it to be controlled by doping with both A and B ions. The lone pair of electrons in Bi^{3+} in the $[Bi_2O_2]^{2+}$ layer plays an important role in controlling valence fluctuations and non-stoichiometric stabilization, giving rise to various physical and chemistry properties. These different physical and chemical properties affect the quality of the Aurivillius material in use for subsequent applications [7], [8]. $ABi_4Ti_4O_{15}$ oxide (A = Ba, Ca, Sr, Pb) is described as orthorhombic [8], [9], [10]. Kojima and Roman (1995) reported that the compound $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Pb) allows cation distortion to occur because there are several *B* ions occupying a random site, such as Bi of the perovskite layer [11]. However, $ABi_4Ti_4O_{15}$ oxide (A = Ba, Ca, Sr) has not been explained by its stability based on the increase in the concentration of dopants which substitute Bi in the perovskite layer. The stability can be viewed from the lattice energy, cell parameters, polarizability, and perovskite tolerance factors, as explained in this study. It also relates to the bond valence sum of an ion in a particular structure [12], but was not done in this study. If doping is based on increasing concentrations and in large amounts, it will require a lot of time and cost so this research is carried out by atomistic simulation.

The atomistic simulation method is strong enough to study thermodynamics and multiscale modeling. Atomic-level simulations involve potential pairs using rigid ion models or shell models that have successfully described the defect properties of many-ion systems. The ion rigid model requires half the parameters compared to the shell model. This ion rigid model is much faster and effective for multiscale simulation. On the other hand, the need for few parameters is challenged to get a valid model for atomic interactions, especially for complex systems. Therefore, atomistic simulations mostly use the shell model framework [13], [14]. This research is an atomistic study of the lattice structure of the four layer Aurivillius oxide of $A_xBi_{4-x}Ti_4O_{15}$ Aurivillius (A = Ca, Sr, and Ba), where *x* is dopant concentration.

MATERIALS AND METHODS

This atomistic simulation is done through a geometry optimization procedure using a Linux-based computer that is equipped with the General Utility lattice Program (GULP) code. Atomistic modeling illustrates the interactions between ions in a crystal structure based on a solid model proposed by Born [15]. Modeling interactions between ions can be understood through the function of potential energy of system, especially the system of two objects that describe these interactions. The potential energy of attraction and repulsion between each ion pair in a solid crystal at zero Kelvin is expressed as a static lattice energy which is formulated as:

$$E_L = \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} \theta_{ij} + \sum_{ijk} \theta_{ijk} \quad (1)$$

The first term of equation (1) is the static lattice energy of the long-range Coulomb's pull for the arrangement of infinite ions. The second term expresses the diffusion properties of the electron cloud surrounding the nucleus consisting of short-range interactions associated with Pauli's repulsion between neighboring electron clouds and van der Waals attraction components of short-range. The third term describes the interaction of three objects, in the solids of ions, the interaction of two objects dominates. In the rigid ion model, the short-range interaction is stimulated mainly by the effects of the nearest neighbor ion. The short-range potential function can be described by the Buckingham potential:

$$\theta_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6} \quad (2)$$

where A_{ij}, ρ_{ij} and C_{ij} are constants and r_{ij} is the distance between ions. The first term in equation (2) represents a short-range repulsion, while the second term shows the pull of induced dipoles (van der Waals).

In addition to the ion interaction model, the model can also include ion polarization descriptions [16]. The model represents the ion as a charged shell with a very small mass (representing the outer valence electron cloud) which is bound to a large mass nucleus by a harmonious spring. Additional energy due to shell interactions with the nucleus is expressed by equation (3):

$$U_s = \sum_i k_i^s r_i^2 \quad (3)$$

where is the spring constant and is the distance between the core and the shell. Equation (3) describes the ion polarization, which is needed for the calculation of the defect energy and the dielectric constant. Ion polarization is formulated by equation (4):

$$\alpha_i = \sum \frac{(Y_i e)^2}{k_i^s} \quad (4)$$

where *Y*i is the shell charge and *e* is the electron charge. Coulomb interaction calculation in this study will use the Ewald method with GULP code. Meanwhile, the short-range potential used is the Buckingham potential [17], [18].

RESULTS AND DISCUSSION

Aurivillius structure is composed of perovskite layer and bismuth layer, $[Bi_2O_2]^{2+}$ which alternates along the c axis. Bi ions in the $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) structure occupy Bi(1) and Bi(2) sites in the perovskite layer and Bi(3) in the bismuth layer, as shown in Figure 1. In this study, substitution Bi by dopant (Ca, Sa, Ba) is done partially at Bi(1) or Bi(2) position based on the increase in dopant concentration. The dopants replace a certain amount of Bi of the perovskite layer, while (at the same time), the concentrations of Bi(3), O^{2-}, and Ti^{4+} ions are allowed to remain. The standard Bi concentration (occupancy) of Aurivillius at the Bi(1) and Bi(2) siets is based on the Aurivillius $ABi_4Ti_4O_{15}$ oxide (Figure 1) reported by Kennedy et al. [8]. Bi occupancy at Bi(1) and Bi(2) sites is 0.81 and 0.83, respectively. That is, Sr (as a dopant) occupy the positions respectively by 0.19 or 19% and 0.17 or 17%. If 20% Bi is substituted by Sr in the Bi(1) site then the fractional part becomes 0.8 Bi(1), 80% and 0.2 Sr(1), 20%. Thus, each Bi substitution in a certain position, with dopants at different concentrations, then the concentration of Bi will change as much as the concentration of dopants entering the site. Instead the concentration of ions in other positions is fixed.

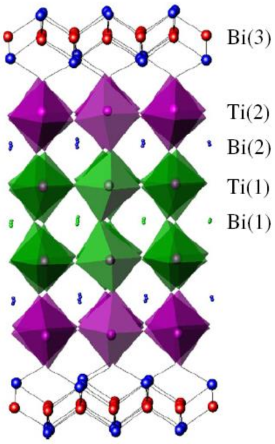

Figure 1 Representation of Arivillius $ABi_4Ti_4O_{15}$ (Ca, Sr, Ba) Oxide Structure (n = 4). Bi(1) and Bi(2) are in the perovskite layer, and Bi(2) is closer to the $[Bi_2O_2]^{2+}$ layer.

Aurivillius of $ABi_4Ti_4O_{15}$ (Ca, Sr, Ba) are atomically simulated at a constant pressure using the GULP code. This simulation is based on lattice minimization which is done iteratively. During this process, the forces on each ion are calculated, and then the ion is shifted slightly in proportion to the forces acting on it. This process continues, until the forces acting on all ions are zero. The simulation in this study is determined by the Buckingham potential and the charge model (shell model) of the Aurivillius oxide. Potential Buckingham (short-range) and shell models (based on atomistic simulation results) suitable for Aurivillius $ABi_4Ti_4O_{15}$ oxide (Ca, Sr, Ba) are shown in Table 1.

Tabel 1. Buckingham potential (short-range) and shell model of ions from Aurivillius ABi4Ti4O15 oxide (Ca, Sr, Ba)

a) *Short-range*	*A* (eV)	*r* (Å)	(eV Å^{-6})
Bi^{3+}...O^{2-}	49.529,35	0,2223	0,0
Ca^{2+}...O^{2-}	1186,6	0,2970	0,0
Sr^{2+}...O^{2-}	1956,702	0,3252	0,0
Ba^{2+}...O^{2-}	4818,416	0,3067	0,0
O^{2-}...O^{2-}	576,940	0,33236	0,0

b) *Shell model*

Species	*k* (eV Å^{-2})	*Shell*(e)
Bi^{3+}	359,55	-5,51
Ti^{4+}	253,60	1,678
Ca^{2+}	34,05	1,281
Sr^{2+}	21,53	1,831
Ba^{2+}	34,0	1,831
O^{2-}	70,1512	-2,04

The ease of polarized dopants can be determined by charge of shell and the spring constant (polarizability). The shell charges of Sr and Ba are the same, but the spring constant is different, whereas Ca and Ba have the same spring constant, but the charge is different. The difference in the charge of the shell or the spring constant shows that the ease of dopant ions is polarized (polarizability) also different. The results of simulation show that the Sr> Ba> Ca polarizabilities as shown in Figure 2. However, in theory the smaller the ionic radius, the weaker the ionized is polarized by anions (oxygen), so the ease of the Ca, Sr, and Ba ions polarized oxygen is Ba> Sr> Ca. Differences in theoretical polarization and simulation results differ between Ba and Sr, where the simulation results show that Sr is more easily polarized than Ba. This is caused by the weak bond between the nucleus of the atom and the electrons as shown by the small Sr spring constant, 21 (eV Å^{-2}).

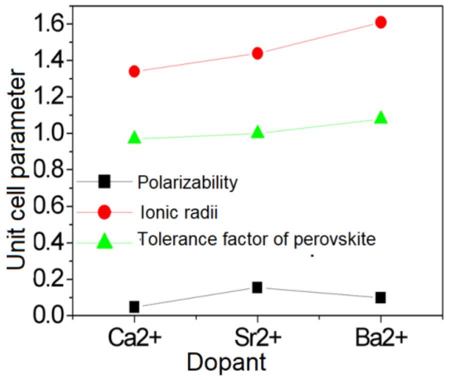

Figure 2 Polarizabilities, ionic radii, and perovskite tolerance factors of Aurivillius $ABi_4Ti_4O_{15}$ oxide (Ca, Sr, Ba).

The polarizability shows that the structure of $ABi_4Ti_4O_{15}$ experienced greater distortion compared to the Aurivillius $ABi_4Ti_4O_{15}$ (A = Ca, Ba). The cell parameters of *a* and *b* of $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) have increased along with the increase in the concentration of dopants that partially substitution Bi

both in Bi(1) and Bi (2) sites. Conversely, the value of *c* changes (increases or decreases); Bi substitution by dopant in position Bi(1), then the value of *c* decreases, conversely substitution of Bi in site of Bi(2), then the value of *c* increases (except substitution with dopant Ca). The increase in the value of *c* is probably caused by the effect of repulsion of the pair of free electrons Bi which is in t $[Bi_2O_2]^{2+}$ layer. The site of Bi(2) is closer to the bismuth layer, so that the repulsion of the electron pair will be strong to the ions which are in site (2) of the perovskite layer. In addition, the more easily polarized Sr and Ba ions cause a small increase in the *a* and *b* values of the $ABi_4Ti_4O_{15}$ structure (A = Sr, Ba). However, the decrease in *c* value in $CaBi_4Ti_4O_{15}$ (Bi is substituted with Ca in Bi(2) site is probably caused by Ca ions which are not easily hard polarized oxygen.

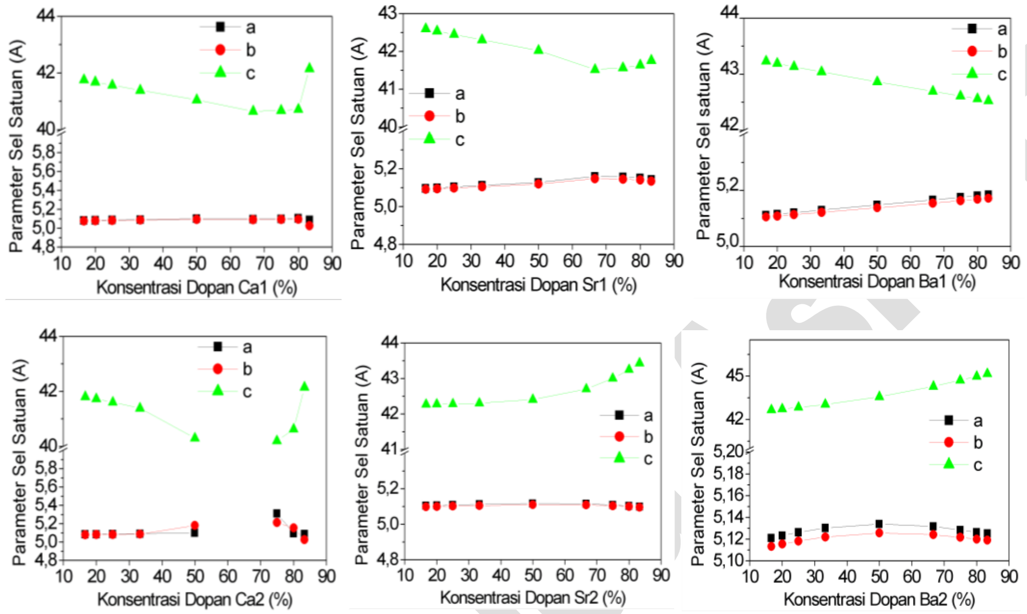

Figure 3 $ABi_4Ti_4O_{15}$ unit cell parameters (A = Ca, Sr, Ba); the values of a and b increase with increasing dopant concentration, but the value of c decreases when substituting in position Bi (1) and increases when substitution in position Bi (2).

The stability of the perovskite structure can be predicted also by the tolerance factor of perovskite (t) proposed by Goldschmidt. This measures the size mismatch between cations A and B in the perovskite. The tolerance factor is defined as $t = (\langle r_A \rangle + r_{O)}/\sqrt{2}(r_{B+}\, r_O$, where $\langle r_A \rangle$ is the average radius of cation A with dodecahderal coordination, r_B- ionic radius of cation B with 6-coordinate, r_O- oxygen radius of octahedral coordination [19]. When it is equal to unity, it is related to an undistorted ideal perovskite, while *t* <1 has a distorted perovskite system that shows the tilt or rotation of the octahedral BO_6. The perovskite layer of $ABi_4Ti_4O_{15}$ with that is doped with distortion because t is not equal to 1. It is Ba who has the highest level of distortion, with a tolerance factor far above one compared to the t value for Ca and Sr. Sr which is almost the same as one has less slope compared to the other.

This result is different from the report of Reaney et al. (1994) which shows that perovskite at room temperature with 0.985 <*t*<1.06 is expected to have undistorted. Perovskites with 0.964 <*t*<0.985 typically have anti-phase slant structures and perovskites with t <0.964 are expected to show phase-and anti-phase tilting [20], [21]. As *t* continues to decline, the stability of the perovskite system decreases and eventually does not form. This is understandable because the consideration is the radius of the Shannon ion Bi^{3+} (r = 1.17 Å) in 8-fold coordination, with *t* going to be 0.8886 [22]. Therefore. Perovskite structure is not stable. However, if we consider that the Bi^{3+} ion is dodecahedral coordination with ionic radius of 1.40 Å, then the t value indicates the distortion of BO6 of $ABi_4Ti_4O_{15}$ doped with Ca^{2+}, Sr^{2+}, and Ba^{2+} to partially substitute Bi in the perovskite layer. This was also observed in $BiFeO_3$ with *t* value of 0.96 [23]–[25]. Thus the cation A size variance and tolerance factor (t) are also the factors responsible for the formation of perovskite octahedral distortion.

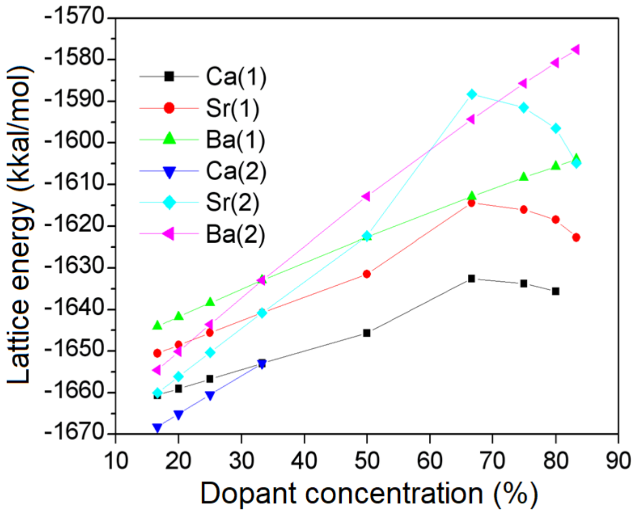

Figure 4. $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) lattice energy with dopant concentration; Bi (1) and Bi (2) substitution by dopant is done partially based on the increase in dopant concentration.

The greater the concentration of dopant, the doped Aurivillius lattice energy is greater, according to the increase in dopant ion radius ($r_{Ca} < r_{Sr} < r_{Ba}$, 1.34, 1.44, 1.61) [24]. $ABi_4Ti_4O_{15}$ Aurivillius is more stable when substitution of Bi by dopants in position 2 of Bi(2) with dopant concentrations below 33.3%. Conversely, dopant concentration values above that, the Bi substitution is more stable at site Bi(1). Bi substitution is easier in the perovskite layer compared to the bismuth oxide layer. In addition, the maximum number of dopants that substitute Bi is only around 33% in the bismuth layer [26]. In the perovskite layer is also a major factor determining the ability of oxygen ions to migrate if the Aurivillius structure is empty [27]. This means that the perovskite layer is more likely to be modified so that Aurvillius can be applied in the ferroelectric, catalyst or electrolyte industries.

Sadapu *et al* (2015) reported Aurivillius lattice energy doped in the Bi_2O_2 layer was greater than the Aurivillius lattice energy doped in the perovskite layer. The energy lattices of $Ba_xBi_{4-x}Ti_4O_{15}$, $Ca_xBi_{4-x}Ti_4O_{15}$ and $Sr_xBi_{4-x}Ti_4O_{15}$ are 1491,418, -1498,560, and 1494,338 eV, respectively. The maximum concentration of dopants are Ba 33, Ca, 32, Sr 33% [26]. The four coordination that forms the rectangular pyramid (BiO_4) in the bismuth oxide layer causes the small number of dopants to substitute Bi for the layer. Moreover, Bi has a lone pair of electrons which can repel dopant electrons that enter to replace it. Although the length of the Bi-O bond formed is longer because there are free electrons, the bond length is much smaller when dodecahedral coordinates of Bi on the perovskite layer. Therefore, coordination, dopant size, and the presence of free electrons determine the stability of the doped compound structure [28].

CONCLUSION

The unit cell parameters $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) fit well with the experimental unit cell parameters. Increasing dopant concentration which substitutes Bi, then the Aurivillius $ABi_4Ti_4O_{15}$ lattice energy is getting bigger. $ABi_4Ti_4O_{15}$ is more stable when dopant (A) substitutes Bi in Bi(2) position with dopant concentration below 33%. Conversely, dopant concentration above that, the substitution of Bi by dopant A at position Bi(1) is more stable. The maximum limit of Ca dopants substituting Bi(2) is 33%, while other dopants can completely substitute Bi(2). This research can be used as a guide for the synthesis of Aurivillius $ABi_4Ti_4O_{15}$ compounds.

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RESEARCH PAPER

Stability Study of Four Layer Aurivillius Oxide of $A_xBi_{4-x}Ti_4O_{15}$ (A = Ca, Sr, Ba): Atomistic Simulation

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Abstract: ~~Aurivillius is bismuth layered structure ferroelectrics which can be applied as memory, sensor, and catalyst.~~ This research aimed to study the stability of $A_xBi_{4-x}Ti_4O_{15}$ Aurivillius (A = Ca, Sr, and Ba). Dopants (A) partially substitute Bi at the sites of Bi(1) and Bi(2) of perovskite layer. This research method is atomistic simulation using by GULP code. Simulations were carried out by means of $A_xBi_{4-x}Ti_4O_{15}$ geometry optimization at a constant pressure, using the Buckingham potential. The results showed that the increase in the concentration of dopants substituting Bi accompanied with increase in lattice energies. The most stable Aurivillius was $Ca_xBi_{4-x}Ti_4O_{15}$ (x = 16.3%) carried out by Bi substitution at Bi(2) site, with lattice energy, -1668.227 eV. Aurivillius stability decreases by increasing size of the dopant. The maximum concentration number of A dopant substituting Bi was discussed.

Keywords: Aurivillius; ~~A~~atomistic simulation; lattice energy; dopants of earth alkaline ionic; shell model

INTRODUCTION

The specific nature of Aurivillius is determined by its crystal structure [1]. The packaging of the ions in the structure determines type and possibility of Aurivillius application [2]. One of the interesting properties of Aurvillius is ferroelectric which can be applied as a storage material of Fe-RAM memory, capacitors, piezoelectric, conductor, catalyst, and as a magnetic material [3], [4]. To achieve the property, then Aurvillius doped with certain ions on bismuth oxide or perovskite layers.

Aurivillius oxide is an oxide compound with a layered structure that is arranged regularly and alternates between layers of perovskite of $[A_{n-1}B_nO_{3n+1}]^{2-}$ and $[Bi_2O_2]^{2+}$. Cation A is dodecahedral coordinated ions, which have a charge of +1, +2 or +3, such as alkali, earth alkaline, rare earth elements or mixtures. Cation B is ions with octahedral coordination which are usually transition elements with smaller sizes than cation A. While *n* is an integer which shows the octahedral number in the perovskite layer [5], [6].

Layered oxide has structural and composition flexibility that allows it to be controlled by doping with both A and B ions. The lone pair of electrons in Bi^{3+} in the $[Bi_2O_2]^{2+}$ layer plays an important role in controlling valence fluctuations and non-stoichiometric stabilization, giving rise to various physical and chemistry properties. These different physical and chemical properties affect the quality of the Aurivillius material in use for subsequent applications [7], [8]. $ABi_4Ti_4O_{15}$ oxide (A = Ba, Ca, Sr, Pb) is described as orthorhombic [8], [9], [10]. Kojima and Roman (1995) reported that the compound $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Pb) allows cation distortion to occur because there are several *B* ions occupying a random site, such as Bi of the perovskite layer [11]. However, $ABi_4Ti_4O_{15}$ oxide (A = Ba, Ca, Sr) has not been explained by its stability based on the increase in the concentration of dopants which substitute Bi in the perovskite layer. The stability can be viewed from the lattice energy, cell parameters, polarizability, and perovskite tolerance factors, as explained in this study. It also relates to the bond valence sum of an ion in a particular structure [12], but was not done in this study. If doping is based on increasing concentrations and in large amounts, it will require a lot of time and cost so this research is carried out by atomistic simulation.

The atomistic simulation method is strong enough to study thermodynamics and multiscale modeling. Atomic-level simulations involve potential pairs using rigid ion models or shell models that have successfully described the defect properties of many-ion systems. The ion rigid model requires half the parameters compared to the shell model. This ion rigid model is much faster and effective for multiscale simulation. On the other hand, the need for few parameters is challenged to get a valid model for atomic interactions, especially for complex systems. Therefore, atomistic simulations mostly use the shell model framework [13] [14]. This research is an atomistic study of the lattice structure of the four layer Aurivillius oxide of $A_xBi_{4-x}Ti_4O_{15}$ Aurivillius (A = Ca, Sr, and Ba), where *x* is dopant concentration.

MATERIALS AND METHODS

This atomistic simulation is done through a geometry optimization procedure using a Linux-based computer that is equipped with the General Utility lattice Program (GULP) code. Atomistic modeling illustrates the interactions between ions in a crystal structure based on a solid model proposed by Born [15]. Modeling interactions between ions can be understood through the function of potential energy of system, especially the system of two objects that describe these interactions. The potential energy of attraction and repulsion between each ion pair in a solid crystal at zero Kelvin is expressed as a static lattice energy which is formulated as:

$$E_L = \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} \theta_{ij} + \sum_{ijk} \theta_{ijk} \qquad (1)$$

The first term of equation (1) is the static lattice energy of the long-range Coulomb's pull for the arrangement of infinite ions. The second term expresses the diffusion properties of the electron cloud surrounding the nucleus consisting of short-range interactions associated with Pauli's repulsion between neighboring electron clouds and van der Waals attraction components of short-range. The third term describes the interaction of three objects, in the solids of ions, the interaction of two objects dominates. In the rigid ion model, the short-range interaction is stimulated mainly by the effects of the nearest neighbor ion. The short-range potential function can be described by the Buckingham potential:

$$\theta_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \qquad (2)$$

where A_{ij}, ρ_{ij} and C_{ij} are constants and r_{ij} is the distance between ions. The first term in equation (2) represents a short-range repulsion, while the second term shows the pull of induced dipoles (van der Waals).

In addition to the ion interaction model, the model can also include ion polarization descriptions [16]. The model represents the ion as a charged shell with a very small mass (representing the outer valence electron cloud) which is bound to a large mass nucleus by a harmonious spring. Additional energy due to shell interactions with the nucleus is expressed by equation (3):

$$U_s = \sum_i k_i^s r_i^2 \qquad (3)$$

where is the spring constant and is the distance between the core and the shell. Equation (3) describes the ion polarization, which is needed for the calculation of the defect energy and the dielectric constant. Ion polarization is formulated by equation (4):

$$\alpha_i = \sum \frac{(Y_i e)^2}{k_i^s} \qquad (4)$$

where *Y*i is the shell charge and *e* is the electron charge. Coulomb interaction calculation in this study will use the Ewald method with GULP code. Meanwhile, the short-range potential used is the Buckingham potential [17], [18].

RESULTS AND DISCUSSION

Aurivillius structure is composed of perovskite layer and bismuth layer, $[Bi_2O_2]^{2+}$ which alternates along the c axis. Bi ions in the $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) structure occupy Bi(1) and Bi(2) sites in the perovskite layer and Bi(3) in the bismuth layer, as shown in Figure 1. In this study, substitution Bi by dopant (Ca, Sa, Ba) is done partially at Bi(1) or Bi(2) position based on the increase in dopant concentration. The dopants replace a certain amount of Bi of the perovskite layer, while (at the same time), the concentrations of Bi(3), O^{2-}, and Ti^{4+} ions are allowed to remain. The standard Bi concentration (occupancy) of Aurivillius at the Bi(1) and Bi(2) siets is based on the Aurivillius $ABi_4Ti_4O_{15}$ oxide (Figure 1) reported by Kennedy et al. [8]. Bi occupancy at Bi(1) and Bi(2) sites is 0.81 and 0.83, respectively. That is, Sr (as a dopant) occupy the positions respectively by 0.19 or 19% and 0.17 or 17%. If 20% Bi is substituted by Sr in the Bi(1) site then the fractional part becomes 0.8 Bi(1), 80% and 0.2 Sr(1), 20%. Thus, each Bi substitution in a certain position, with dopants at different concentrations, then the concentration of Bi will change as much as the concentration of dopants entering the site. Instead the concentration of ions in other positions is fixed.

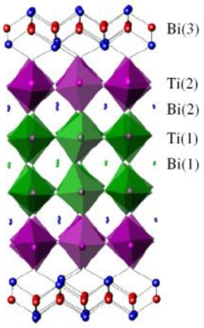

Figure 1. Representation of Arivillius $ABi_4Ti_4O_{15}$ (Ca, Sr, Ba) Oxide Structure (n = 4). Bi(1) and Bi(2) are in the perovskite layer, and Bi(2) is closer to the $[Bi_2O_2]^{2+}$ layer.

Aurivillius of $ABi_4Ti_4O_{15}$ (Ca, Sr, Ba) are atomically simulated at a constant pressure using the GULP code. This simulation is based on lattice minimization which is done iteratively. During this process, the forces on each ion are calculated, and then the ion is shifted slightly in proportion to the forces acting on it. This process continues, until the forces acting on all ions are zero. The simulation in this study is determined by the Buckingham potential and the charge model (shell model) of the Aurivillius oxide. Potential Buckingham (short-range) and shell models (based on atomistic simulation results) suitable for Aurivillius $ABi_4Ti_4O_{15}$ oxide (Ca, Sr, Ba) are shown in Table 1.

Tabel 1. Buckingham potential (short-range) and shell model of ions from Aurivillius ABi4Ti4O15 oxide (Ca, Sr, Ba)

a) *Short-range*	*A* (eV)	*r* (Å)	(eV Å^{-6})
Bi^{3+}...O^{2-}	49.529,35	0,2223	0,0
Ca^{2+}...O^{2-}	1186,6	0,2970	0,0
Sr^{2+}...O^{2-}	1956,702	0,3252	0,0
Ba^{2+}...O^{2-}	4818,416	0,3067	0,0
O^{2-}...O^{2-}	576,940	0,33236	0,0

b) *Shell model*

Species	*k* (eV Å^{-2})	*Shell*(e)
Bi^{3+}	359,55	-5,51
Ti^{4+}	253,60	1,678
Ca^{2+}	34,05	1,281
Sr^{2+}	21,53	1,831
Ba^{2+}	34,0	1,831
O^{2-}	70,1512	-2,04

The ease of polarized dopants can be determined by charge of shell and the spring constant (polarizability). The shell charges of Sr and Ba are the same, but the spring constant is different, whereas Ca and Ba have the same spring constant, but the charge is different. The difference in the charge of the shell or the spring constant shows that the ease of dopant ions is polarized (polarizability) also different. The results of simulation show that the Sr> Ba> Ca polarizabilities as shown in Figure 2. However, in theory the smaller the ionic radius, the weaker the ionized is polarized by anions (oxygen), so the ease of the Ca, Sr, and Ba ions polarized oxygen is Ba> Sr> Ca. Differences in theoretical polarization and simulation results differ between Ba and Sr, where the simulation results show that Sr is more easily polarized than Ba. This is caused by the weak bond between the nucleus of the atom and the electrons as shown by the small Sr spring constant, 21 (eV Å^{-2}).

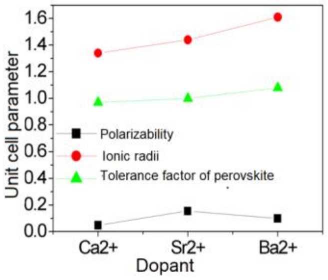

Figure 2. Polarizabilities, ionic radii, and perovskite tolerance factors of Aurivillius $ABi_4Ti_4O_{15}$ oxide (Ca, Sr, Ba).

The polarizability shows that the structure of $ABi_4Ti_4O_{15}$ experienced greater distortion compared to the Aurivillius $ABi_4Ti_4O_{15}$ (A = Ca, Ba). The cell parameters of *a* and *b* of $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) have increased along with the increase in the concentration of dopants that partially substitution Bi

both in Bi(1) and Bi (2) sites. Conversely, the value of *c* changes (increases or decreases); Bi substitution by dopant in position Bi(1), then the value of *c* decreases, conversely substitution of Bi in site of Bi(2), then the value of *c* increases (except substitution with dopant Ca). The increase in the value of *c* is probably caused by the effect of repulsion of the pair of free electrons Bi which is in t $[Bi_2O_2]^{2+}$ layer. The site of Bi(2) is closer to the bismuth layer, so that the repulsion of the electron pair will be strong to the ions which are in site (2) of the perovskite layer. In addition, the more easily polarized Sr and Ba ions cause a small increase in the *a* and *b* values of the $ABi_4Ti_4O_{15}$ structure (A = Sr, Ba). However, the decrease in *c* value in $CaBi_4Ti_4O_{15}$ (Bi is substituted with Ca in Bi(2) site is probably caused by Ca ions which are not easily hard polarized oxygen.

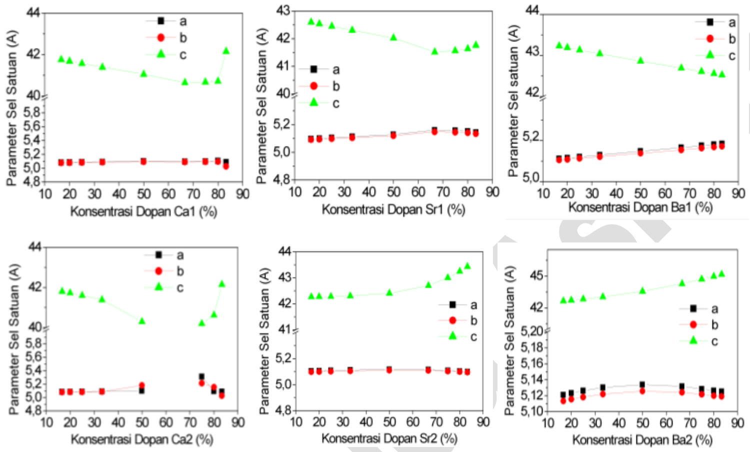

Figure 3. $ABi_4Ti_4O_{15}$ unit cell parameters (A = Ca, Sr, Ba); the values of a and b increase with increasing dopant concentration, but the value of c decreases when substituting in position Bi (1) and increases when substitution in position Bi (2).

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The stability of the perovskite structure can be predicted also by the tolerance factor of perovskite (t) proposed by Goldschmidt. This measures the size mismatch between cations A and B in the perovskite. The tolerance factor is defined as $t = (\langle r_A \rangle + r_{O)} / \sqrt{2}(r_{B+}\, r_O$, where $\langle r_A \rangle$ is the average radius of cation A with dodecahderal coordination, r_B- ionic radius of cation B with 6-coordinate, r_O- oxygen radius of octahedral coordination [19]. When it is equal to unity, it is related to an undistorted ideal perovskite, while *t* <1 has a distorted perovskite system that shows the tilt or rotation of the octahedral BO_6. The perovskite layer of $ABi_4Ti_4O_{15}$ with that is doped with distortion because t is not equal to 1. It is Ba who has the highest level of distortion, with a tolerance factor far above one compared to the t value for Ca and Sr. Sr which is almost the same as one has less slope compared to the other.

This result is different from the report of Reaney et al. (1994) which shows that perovskite at room temperature with 0.985 <*t*<1.06 is expected to have undistorted. Perovskites with 0.964 <*t*<0.985 typically have anti-phase slant structures and perovskites with t <0.964 are expected to show phase-and anti-phase tilting [20], [21]. As *t* continues to decline, the stability of the perovskite system decreases and eventually does not form. This is understandable because the consideration is the radius of the Shannon ion Bi^{3+} (r = 1.17 Å) in 8-fold coordination, with *t* going to be 0.8886 [22]. Therefore. Perovskite structure is not stable. However, if we consider that the Bi^{3+} ion is dodecahedral coordination with ionic radius of 1.40 Å, then the t value indicates the distortion of BO6 of $ABi_4Ti_4O_{15}$ doped with Ca^{2+}, Sr^{2+}, and Ba^{2+} to partially substitute Bi in the perovskite layer. This was also observed in $BiFeO_3$ with *t* value of 0.96 [23]–[25]. Thus the cation A size variance and tolerance factor (t) are also the factors responsible for the formation of perovskite octahedral distortion.

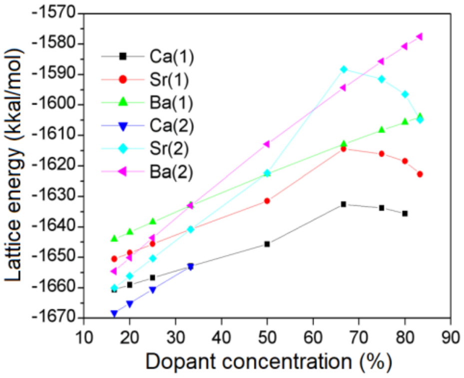

Figure 4. $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) lattice energy with dopant concentration; Bi (1) and Bi (2) substitution by dopant is done partially based on the increase in dopant concentration.

The greater the concentration of dopant, the doped Aurivillius lattice energy is greater, according to the increase in dopant ion radius ($r_{Ca} < r_{Sr} < r_{Ba}$, 1.34, 1.44, 1.61) [24]. $ABi_4Ti_4O_{15}$ Aurivillius is more stable when substitution of Bi by dopants in position 2 of Bi(2) with dopant concentrations below 33.3%. Conversely, dopant concentration values above that, the Bi substitution is more stable at site Bi(1). Bi substitution is easier in the perovskite layer compared to the bismuth oxide layer. In addition, the maximum number of dopants that substitute Bi is only around 33% in the bismuth layer [26]. In the perovskite layer is also a major factor determining the ability of oxygen ions to migrate if the Aurivillius structure is empty [27]. This means that the perovskite layer is more likely to be modified so that Aurvillius can be applied in the ferroelectric, catalyst or electrolyte industries.

Sadapu *et al*. (2015) reported Aurivillius lattice energy doped in the Bi_2O_2 layer was greater than the Aurivillius lattice energy doped in the perovskite layer. The energy lattices of $Ba_xBi_{4-x}Ti_4O_{15}$, $Ca_xBi_{4-x}Ti_4O_{15}$ and $Sr_xBi_{4-x}Ti_4O_{15}$ are 1491,418, -1498,560, and 1494,338 eV, respectively. The maximum concentration of dopants are Ba 33, Ca, 32, Sr 33% [26]. The four coordination that forms the rectangular pyramid (BiO_4) in the bismuth oxide layer causes the small number of dopants to substitute Bi for the layer. Moreover, Bi has a lone pair of electrons which can repel dopant electrons that enter to replace it. Although the length of the Bi-O bond formed is longer because there are free electrons, the bond length is much smaller when dodecahedral coordinates of Bi on the perovskite layer. Therefore, coordination, dopant size, and the presence of free electrons determine the stability of the doped compound structure [28].

CONCLUSION

The unit cell parameters $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) fit well with the experimental unit cell parameters. Increasing dopant concentration which substitutes Bi, then the Aurivillius $ABi_4Ti_4O_{15}$ lattice energy is getting bigger. $ABi_4Ti_4O_{15}$ is more stable when dopant (A) substitutes Bi in Bi(2) position with dopant concentration below 33%. Conversely, dopant concentration above that, the substitution of Bi by dopant A at position Bi(1) is more stable. The maximum limit of Ca dopants substituting Bi(2) is 33%, while other dopants can completely substitute Bi(2). This research can be used as a guide for the synthesis of Aurivillius $ABi_4Ti_4O_{15}$ compounds.

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RESEARCH PAPER

Stability Study of Four Layer Aurivillius Oxide of $A_xBi_{4-x}Ti_4O_{15}$ (A = Ca, Sr, Ba): Atomistic Simulation

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Abstract: This research aimed to study the stability of $A_xBi_{4-x}Ti_4O_{15}$ Aurivillius (A = Ca, Sr, and Ba). Dopants (A) partially substitute Bi at the sites of Bi(1) and Bi(2) of perovskite layer. This research method is atomistic simulation using by GULP code. Simulations were carried out by means of $A_xBi_{4-x}Ti_4O_{15}$ geometry optimization at a constant pressure, using the Buckingham potential. The results showed that the increase in the concentration of dopants substituting Bi accompanied with increase in lattice energies. The most stable Aurivillius was $Ca_xBi_{4-x}Ti_4O_{15}$ (x = 16.3%) carried out by Bi substitution at Bi(2) site, with lattice energy, -1668.227 eV. Aurivillius stability decreases by increasing size of the dopant. The maximum concentration number of A dopant substituting Bi was discussed.

Keywords: Aurivillius; atomistic simulation; lattice energy; dopants of earth alkaline ionic; shell model

INTRODUCTION

The specific nature of Aurivillius is determined by its crystal structure [1]. The packaging of the ions in the structure determines type and possibility of Aurivillius application [2]. One of the interesting properties of Aurvillius is ferroelectric which can be applied as a storage material of Fe-RAM memory, capacitors, piezoelectric, conductor, catalyst, and as a magnetic material [3], [4]. To achieve the property, then Aurvillius doped with certain ions on bismuth oxide or perovskite layers.

Aurivillius oxide is an oxide compound with a layered structure that is arranged regularly and alternates between layers of perovskite of $[A_{n-1}B_nO_{3n+1}]^{2-}$ and $[Bi_2O_2]^{2+}$. Cation A is dodecahedral coordinated ions, which have a charge of +1, +2 or +3, such as alkali, earth alkaline, rare earth elements or mixtures. Cation B is ions with octahedral coordination which are usually transition elements with smaller sizes than cation A. While *n* is an integer which shows the octahedral number in the perovskite layer [5], [6].

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Layered oxide has structural and composition flexibility that allows it to be controlled by doping with both A and B ions. The lone pair of electrons in Bi^{3+} in the $[Bi_2O_2]^{2+}$ layer plays an important role in controlling valence fluctuations and non-stoichiometric stabilization, giving rise to various physical and chemistry properties. These different physical and chemical properties affect the quality of the Aurivillius material in use for subsequent applications [7], [8]. $ABi_4Ti_4O_{15}$ oxide (A = Ba, Ca, Sr, Pb) is described as orthorhombic [8], [9], [10]. Kojima and Roman (1995) reported that the compound $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Pb) allows cation distortion to occur because there are several *B* ions occupying a random site, such as Bi of the perovskite layer [11]. However, $ABi_4Ti_4O_{15}$ oxide (A = Ba, Ca, Sr) has not been explained by its stability based on the increase in the concentration of dopants which substitute Bi in the perovskite layer. The stability can be viewed from the lattice energy, cell parameters, polarizability, and perovskite tolerance factors, as explained in this study. It also relates to the bond valence sum of an ion in a particular structure [12], but was not done in this study. If doping is based on increasing concentrations and in large amounts, it will require a lot of time and cost so this research is carried out by atomistic simulation.

The atomistic simulation method is strong enough to study thermodynamics and multiscale modeling. Atomic-level simulations involve potential pairs using rigid ion models or shell models that have successfully described the defect properties of many-ion systems. The ion rigid model requires half the parameters compared to the shell model. This ion rigid model is much faster and effective for multiscale simulation. On the other hand, the need for few parameters is challenged to get a valid model for atomic interactions, especially for complex systems. Therefore, atomistic simulations mostly use the shell model framework [13] [14]. This research is an atomistic study of the lattice structure of the four layer Aurivillius oxide of $A_xBi_{4-x}Ti_4O_{15}$ Aurivillius (A = Ca, Sr, and Ba), where *x* is dopant concentration.

MATERIALS AND METHODS

This atomistic simulation is done through a geometry optimization procedure using a Linux-based computer that is equipped with the General Utility lattice Program (GULP) code. Atomistic modeling illustrates the interactions between ions in a crystal structure based on a solid model proposed by Born [15]. Modeling interactions between ions can be understood through the function of potential energy of system, especially the system of two objects that describe these interactions. The potential energy of attraction and repulsion between each ion pair in a solid crystal at zero Kelvin is expressed as a static lattice energy which is formulated as:

$$E_L = \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} \theta_{ij} + \sum_{ijk} \theta_{ijk} \quad (1)$$

The first term of equation (1) is the static lattice energy of the long-range Coulomb's pull for the arrangement of infinite ions. The second term expresses the diffusion properties of the electron cloud surrounding the nucleus consisting of short-range interactions associated with Pauli's repulsion between neighboring electron clouds and van der Waals attraction components of short-range. The third term describes the interaction of three objects, in the solids of ions, the interaction of two objects dominates. In the rigid ion model, the short-range interaction is stimulated mainly by the effects of the nearest neighbor ion. The short-range potential function can be described by the Buckingham potential:

$$\theta_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (2)$$

where A_{ij}, ρ_{ij} and C_{ij} are constants and r_{ij} is the distance between ions. The first term in equation (2) represents a short-range repulsion, while the second term shows the pull of induced dipoles (van der Waals).

In addition to the ion interaction model, the model can also include ion polarization descriptions [16]. The model represents the ion as a charged shell with a very small mass (representing the outer valence electron cloud) which is bound to a large mass nucleus by a harmonious spring. Additional energy due to shell interactions with the nucleus is expressed by equation (3):

$$U_s = \sum_i k_i^s r_i^2 \quad (3)$$

where is the spring constant and is the distance between the core and the shell. Equation (3) describes the ion polarization, which is needed for the calculation of the defect energy and the dielectric constant. Ion polarization is formulated by equation (4):

$$\alpha_i = \sum \frac{(Y_i e)^2}{k_i^s} \quad (4)$$

where *Y*i is the shell charge and *e* is the electron charge. Coulomb interaction calculation in this study will use the Ewald method with GULP code. Meanwhile, the short-range potential used is the Buckingham potential [17], [18].

RESULTS AND DISCUSSION

Aurivillius structure is composed of perovskite layer and bismuth layer, $[Bi_2O_2]^{2+}$ which alternates along the c axis. Bi ions in the $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) structure occupy Bi(1) and Bi(2) sites in the perovskite layer and Bi(3) in the bismuth layer, as shown in Figure 1. In this study, substitution Bi by dopant (Ca, Sa, Ba) is done partially at Bi(1) or Bi(2) position based on the increase in dopant concentration. The dopants replace a certain amount of Bi of the perovskite layer, while (at the same time), the concentrations of Bi(3), O^{2-}, and Ti^{4+} ions are allowed to remain. The standard Bi concentration (occupancy) of Aurivillius at the Bi(1) and Bi(2) siets is based on the Aurivillius $ABi_4Ti_4O_{15}$ oxide (Figure 1) reported by Kennedy et al. [8]. Bi occupancy at Bi(1) and Bi(2) sites is 0.81 and 0.83, respectively. That is, Sr (as a dopant) occupy the positions respectively by 0.19 or 19% and 0.17 or 17%. If 20% Bi is substituted by Sr in the Bi(1) site then the fractional part becomes 0.8 Bi(1), 80% and 0.2 Sr(1), 20%. Thus, each Bi substitution in a certain position, with dopants at different concentrations, then the concentration of Bi will change as much as the concentration of dopants entering the site. Instead the concentration of ions in other positions is fixed.

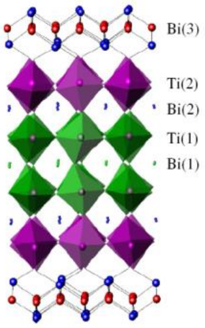

Figure 1. Representation of Arivillius $ABi_4Ti_4O_{15}$ (Ca, Sr, Ba) Oxide Structure (n = 4). Bi(1) and Bi(2) are in the perovskite layer, and Bi(2) is closer to the $[Bi_2O_2]^{2+}$ layer.

Aurivillius of $ABi_4Ti_4O_{15}$ (Ca, Sr, Ba) are atomically simulated at a constant pressure using the GULP code. This simulation is based on lattice minimization which is done iteratively. During this process, the forces on each ion are calculated, and then the ion is shifted slightly in proportion to the forces acting on it. This process continues, until the forces acting on all ions are zero. The simulation in this study is determined by the Buckingham potential and the charge model (shell model) of the Aurivillius oxide. Potential Buckingham (short-range) and shell models (based on atomistic simulation results) suitable for Aurivillius $ABi_4Ti_4O_{15}$ oxide (Ca, Sr, Ba) are shown in Table 1.

Tabel 1. Buckingham potential (short-range) and shell model of ions from Aurivillius ABi4Ti4O15 oxide (Ca, Sr, Ba)

a) *Short-range*	*A* (eV)	*r* (Å)	(eV $Å^{-6}$)
$Bi^{3+}...O^{2-}$	49.529,35	0,2223	0,0
$Ca^{2+}...O^{2-}$	1186,6	0,2970	0,0
$Sr^{2+}...O^{2-}$	1956,702	0,3252	0,0
$Ba^{2+}...O^{2-}$	4818,416	0,3067	0,0
$O^{2-}...O^{2-}$	576,940	0,33236	0,0

b) *Shell model*

Species	*k* (eV $Å^{-2}$)	*Shell*(e)
Bi^{3+}	359,55	-5,51
Ti^{4+}	253,60	1,678
Ca^{2+}	34,05	1,281
Sr^{2+}	21,53	1,831
Ba^{2+}	34,0	1,831
O^{2-}	70,1512	-2,04

The ease of polarized dopants can be determined by charge of shell and the spring constant (polarizability). The shell charges of Sr and Ba are the same, but the spring constant is different, whereas Ca and Ba have the same spring constant, but the charge is different. The difference in the charge of the shell or the spring constant shows that the ease of dopant ions is polarized (polarizability) also different. The results of simulation show that the Sr> Ba> Ca polarizabilities as shown in Figure 2. However, in theory the smaller the ionic radius, the weaker the ionized is polarized by anions (oxygen), so the ease of the Ca, Sr, and Ba ions polarized oxygen is Ba> Sr> Ca. Differences in theoretical polarization and simulation results differ between Ba and Sr, where the simulation results show that Sr is more easily polarized than Ba. This is caused by the weak bond between the nucleus of the atom and the electrons as shown by the small Sr spring constant, 21 (eV $Å^{-2}$).

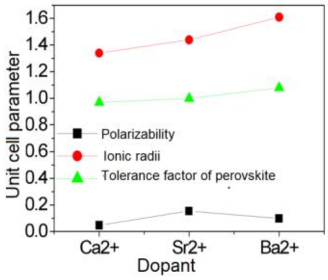

Figure 2. Polarizabilities, ionic radii, and perovskite tolerance factors of Aurivillius $ABi_4Ti_4O_{15}$ oxide (Ca, Sr, Ba).

The polarizability shows that the structure of $ABi_4Ti_4O_{15}$ experienced greater distortion compared to the Aurivillius $ABi_4Ti_4O_{15}$ (A = Ca, Ba). The cell parameters of *a* and *b* of $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) have increased along with the increase in the concentration of dopants that partially substitution Bi

both in Bi(1) and Bi (2) sites. Conversely, the value of *c* changes (increases or decreases); Bi substitution by dopant in position Bi(1), then the value of *c* decreases, conversely substitution of Bi in site of Bi(2), then the value of *c* increases (except substitution with dopant Ca). The increase in the value of *c* is probably caused by the effect of repulsion of the pair of free electrons Bi which is in t $[Bi_2O_2]^{2+}$ layer. The site of Bi(2) is closer to the bismuth layer, so that the repulsion of the electron pair will be strong to the ions which are in site (2) of the perovskite layer. In addition, the more easily polarized Sr and Ba ions cause a small increase in the *a* and *b* values of the $ABi_4Ti_4O_{15}$ structure (A = Sr, Ba). However, the decrease in *c* value in $CaBi_4Ti_4O_{15}$ (Bi is substituted with Ca in Bi(2) site is probably caused by Ca ions which are not easily hard polarized oxygen.

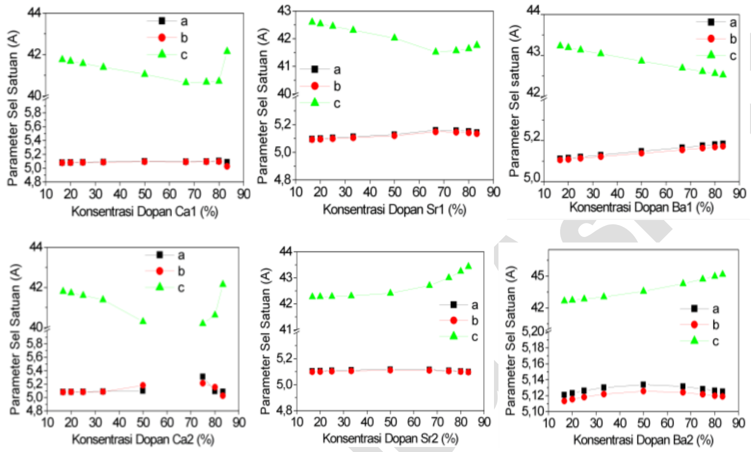

Figure 3. $ABi_4Ti_4O_{15}$ unit cell parameters (A = Ca, Sr, Ba); the values of a and b increase with increasing dopant concentration, but the value of c decreases when substituting in position Bi (1) and increases when substitution in position Bi (2).

The stability of the perovskite structure can be predicted also by the tolerance factor of perovskite (t) proposed by Goldschmidt. This measures the size mismatch between cations A and B in the perovskite. The tolerance factor is defined as $t = (\langle r_A \rangle + r_{O)}/\sqrt{2}(r_{B+}\ r_O$, where $\langle r_A \rangle$ is the average radius of cation A with dodecahderal coordination, r_B- ionic radius of cation B with 6-coordinate, r_O- oxygen radius of octahedral coordination [19]. When it is equal to unity, it is related to an undistorted ideal perovskite, while *t* <1 has a distorted perovskite system that shows the tilt or rotation of the octahedral BO_6. The perovskite layer of $ABi_4Ti_4O_{15}$ with that is doped with distortion because t is not equal to 1. It is Ba who has the highest level of distortion, with a tolerance factor far above one compared to the t value for Ca and Sr. Sr which is almost the same as one has less slope compared to the other.

This result is different from the report of Reaney et al. (1994) which shows that perovskite at room temperature with 0.985 <*t*<1.06 is expected to have undistorted. Perovskites with 0.964 <*t*<0.985 typically have anti-phase slant structures and perovskites with t <0.964 are expected to show phase-and anti-phase tilting [20], [21]. As *t* continues to decline, the stability of the perovskite system decreases and eventually does not form. This is understandable because the consideration is the radius of the Shannon ion Bi^{3+} (r = 1.17 Å) in 8-fold coordination, with *t* going to be 0.8886 [22]. Therefore. Perovskite structure is not stable. However, if we consider that the Bi^{3+} ion is dodecahedral coordination with ionic radius of 1.40 Å, then the t value indicates the distortion of BO6 of $ABi_4Ti_4O_{15}$ doped with Ca^{2+}, Sr^{2+}, and Ba^{2+} to partially substitute Bi in the perovskite layer. This was also observed in $BiFeO_3$ with *t* value of 0.96 [23]–[25]. Thus the cation A size variance and tolerance factor (t) are also the factors responsible for the formation of perovskite octahedral distortion.

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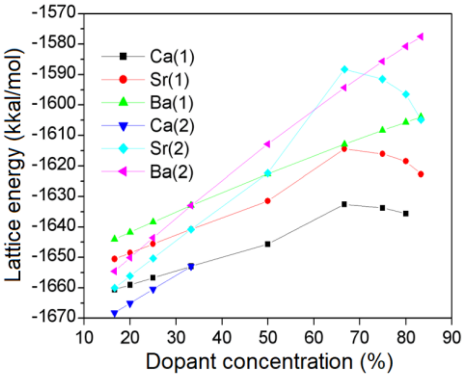

Figure 4. $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) lattice energy with dopant concentration; Bi (1) and Bi (2) substitution by dopant is done partially based on the increase in dopant concentration.

The greater the concentration of dopant, the doped Aurivillius lattice energy is greater, according to the increase in dopant ion radius ($r_{Ca} < r_{Sr} < r_{Ba}$, 1.34, 1.44, 1.61) [24]. $ABi_4Ti_4O_{15}$ Aurivillius is more stable when substitution of Bi by dopants in position 2 of Bi(2) with dopant concentrations below 33.3%. Conversely, dopant concentration values above that, the Bi substitution is more stable at site Bi(1). Bi substitution is easier in the perovskite layer compared to the bismuth oxide layer. In addition, the maximum number of dopants that substitute Bi is only around 33% in the bismuth layer [26]. In the perovskite layer is also a major factor determining the ability of oxygen ions to migrate if the Aurivillius structure is empty [27]. This means that the perovskite layer is more likely to be modified so that Aurvillius can be applied in the ferroelectric, catalyst or electrolyte industries.

Sadapu *et al.* (2015) reported Aurivillius lattice energy doped in the Bi_2O_2 layer was greater than the Aurivillius lattice energy doped in the perovskite layer. The energy lattices of $Ba_xBi_{4-x}Ti_4O_{15}$, $Ca_xBi_{4-x}Ti_4O_{15}$ and $Sr_xBi_{4-x}Ti_4O_{15}$ are 1491,418, -1498,560, and 1494,338 eV, respectively. The maximum concentration of dopants are Ba 33, Ca, 32, Sr 33% [26]. The four coordination that forms the rectangular pyramid (BiO_4) in the bismuth oxide layer causes the small number of dopants to substitute Bi for the layer. Moreover, Bi has a lone pair of electrons which can repel dopant electrons that enter to replace it. Although the length of the Bi-O bond formed is longer because there are free electrons, the bond length is much smaller when dodecahedral coordinates of Bi on the perovskite layer. Therefore, coordination, dopant size, and the presence of free electrons determine the stability of the doped compound structure [28].

CONCLUSION

The unit cell parameters $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) fit well with the experimental unit cell parameters. Increasing dopant concentration which substitutes Bi, then the Aurivillius $ABi_4Ti_4O_{15}$ lattice energy is getting bigger. $ABi_4Ti_4O_{15}$ is more stable when dopant (A) substitutes Bi in Bi(2) position with dopant concentration below 33%. Conversely, dopant concentration above that, the substitution of Bi by dopant A at position Bi(1) is more stable. The maximum limit of Ca dopants substituting Bi(2) is 33%, while other dopants can completely substitute Bi(2). This research can be used as a guide for the synthesis of Aurivillius $ABi_4Ti_4O_{15}$ compounds.

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RESEARCH PAPER

Stability Study of Four Layer Aurivillius Oxide of $A_xBi_{4-x}Ti_4O_{15}$ (A = Ca, Sr, Ba): Atomistic Simulations

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Abbreviations:
GULP: General Utility Lattice Program

Abstract: This research aimed to study the stability of $A_xBi_{4-x}Ti_4O_{15}$ Aurivillius (A = Ca, Sr, and Ba). Dopants (A) partially substitute Bi at the sites of Bi(1) and Bi(2) of the perovskite layer. This research method is an atomistic simulation using the GULP code. Simulations were carried out utilizing $A_xBi_{4-x}Ti_4O_{15}$ geometry optimization at constant pressure, using the Buckingham potential. The results showed that the increase in the concentration of dopants substituting Bi accompanied by an increase in lattice energies. The most stable Aurivillius was $Ca_xBi_{4-x}Ti_4O_{15}$ (x = 16.3%) carried out by Bi substitution at Bi(2) site, with lattice energy, -1668.227 eV. Aurivillius stability decreases by increasing the size of the dopant. The maximum concentration number of A dopant substituting Bi was discussed.

Keywords: atomistic simulation, Aurivillius, dopants of earth alkaline ionic, lattice energy,

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INTRODUCTION

The specific nature of Aurivillius is determined by its crystal structure [1]. The ions in the structure's packaging determine the type and possibility of the Aurivillius application [2]. One of the exciting properties of Aurvillius is ferroelectric, which can be applied as a storage material of Fe-RAM memory, capacitors, piezoelectric, conductor, catalyst, and as a magnetic material [3], [4]. To achieve the property, then Aurvillius doped with specific ions on bismuth oxide or perovskite layers. The introduction should briefly explain the general context and the importance of the reviewed research field. The current state of the research field should be comprehensively reviewed and cited in the key publications.

Aurivillius oxide is an oxide compound with a layered structure arranged regularly and alternates between layers of perovskite of $[A_{n-1}B_nO_{3n+1}]^{2-}$ and $[Bi_2O_2]^{2+}$. Cation A is dodecahedral coordinated ions with a charge of +1, +2, or +3, such as alkali, earth alkaline, rare earth elements, or mixtures. Cation B is ions with octahedral coordination, usually transition elements with smaller sizes than cation A, whereas *n* is an integer which shows the octahedral number in the perovskite layer [5], [6].

Layered oxide has structural and composition flexibility that allows it to be controlled by doping with both A and B ions. The lone pair of electrons in Bi^{3+} in the $[Bi_2O_2]^{2+}$ layer plays an essential role in controlling valence fluctuations and non-stoichiometric stabilization, giving rise to various physical and chemical properties. These different physical and chemical properties affect the quality of the Aurivillius material in use for subsequent applications [7], [8].

$ABi_4Ti_4O_{15}$ oxide (A = Ba, Ca, Sr, Pb) is described as orthorhombic [8], [9], [10]. Kojima and Roman (1995) reported that the compound $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Pb) allows cation distortion to occur because several B ions are occupying a random site, such as Bi of the perovskite layer [11]. However, $ABi_4Ti_4O_{15}$ oxide (A = Ba, Ca, Sr) has not been explained by its stability based on the increase in dopants' concentration, which substitutes Bi in the perovskite layer. The stability can be viewed from the lattice energy, cell parameters, polarizability, and perovskite tolerance factors, as explained in this study. It also relates to the bond valence sum of an ion in a particular structure [12] but was not done in this study. If doping is based on increasing concentrations and large amounts, it will require a lot of time and cost, so this research is carried out by atomistic simulation.

The atomistic simulation method is strong enough to study thermodynamics and multiscale modeling. Atomic-level simulations involve potential pairs using rigid ion models or shell models that have successfully described multiple-ion systems' defect properties. The ion rigid model requires half the parameters compared to the shell model. This ion rigid model is much faster and useful for multiscale simulation. On the other hand, few parameters are challenged to get a valid model for atomic interactions, especially for complex systems. Therefore, atomistic simulations mostly use the shell model framework [13] [14]. This research is an atomistic study of the lattice structure of the four-layer Aurivillius oxide of $A_xBi_{4-x}Ti_4O_{15}$ Aurivillius (A = Ca, Sr, and Ba), where x is dopant concentration.

MATERIALS AND METHODS

This atomistic simulation is done through a geometry optimization procedure using a Linux-based computer equipped with the General Utility Lattice Program (GULP) code. Atomistic modeling illustrates the interactions between ions in a crystal structure based on a solid model proposed by Born [15]. Modeling interactions between ions can be understood through the function of the system's potential energy, especially the system of two objects that describe these interactions. The potential energy of attraction and repulsion between each ion pair in a solid crystal at zero Kelvin is expressed as a static lattice energy, which is formulated as:

$$E_L = \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} \theta_{ij} + \sum_{ijk} \theta_{ijk} \qquad (1)$$

The first term of equation (1) is the static lattice energy of the long-range Coulomb's pull to arrange infinite ions. The second term expresses the electron cloud's diffusion properties surrounding the nucleus consisting of short-range interactions associated with Pauli's repulsion between neighboring electron clouds and van der Waals attraction components of short-range. The third term describes the interaction of three objects, in the solids of ions, the interaction of two objects dominates. In the rigid ion model, the short-range interaction is stimulated mainly by the nearest neighbor ion's effects. The Buckingham potential can describe the short-range potential function:

$$\theta_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6} \qquad (2)$$

where A_{ij}, ρ_{ij}, and C_{ij} are constants, and r_{ij} is the distance between ions. The first term in equation (2) represents a short-range repulsion, while the second term shows the pull of induced dipoles (van der Waals).

In addition to the ion interaction model, the model can also include ion polarization descriptions [16]. The model represents the ion as a charged shell with a tiny mass (representing the outer valence electron cloud), which is bound to a large mass nucleus by a harmonious spring. Additional energy due to shell interactions with the nucleus is expressed by equation (3):

$$U_s = \sum_i k_i^s r_i^2 \qquad (3)$$

where is the spring constant and is the distance between the core and the shell. Equation (3) describes the ion polarization, which is needed for the calculation of the defect energy and the dielectric constant. Ion polarization is formulated by equation (4):

$$\alpha_i = \sum \frac{(Y_i e)^2}{k_i^s} \qquad (4)$$

where Yi is the shell charge, and e is the electron charge. Coulomb interaction calculation in this study will use the Ewald method with the GULP code. Meanwhile, the short-range potential used is the Buckingham potential [17], [18].

RESULTS AND DISCUSSION

Aurivillius structure is composed of a perovskite layer and a bismuth layer, $[Bi_2O_2]^{2+,}$ which alternates along the c axis. Bi ions in the $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) structure occupy Bi(1) and Bi(2) sites in the perovskite layer and Bi(3) in the bismuth layer, as shown in Figure 1. In this study, substitution Bi by dopant (Ca, Sa, Ba) is done partially at Bi(1) or Bi(2) position based on the increase in dopant concentration. The dopants replace a certain amount of Bi of the perovskite layer, while (at the same time) the concentrations of Bi(3), O2-, and Ti4+ ions are allowed to remain. The standard Bi concentration (occupancy) of Aurivillius at the Bi(1) and Bi(2) sites is based on the Aurivillius $ABi_4Ti_4O_{15}$ oxide (Figure 1) reported by Kennedy *et al*. [8]. Bi occupancy at Bi(1) and Bi(2) sites is 0.81 and 0.83, respectively. That is, Sr (as a dopant) occupy the positions respectively by 0.19 or 19% and 0.17 or 17%. If 20% Bi is substituted by Sr in the Bi(1) site then the fractional part becomes 0.8 Bi(1), 80% and 0.2 Sr(1), 20%. Thus, each Bi substitution in a certain position, with dopants at different concentrations, then the Bi concentration will change as much as the concentration of dopants entering the site. Instead, the concentration of ions in other positions is fixed.

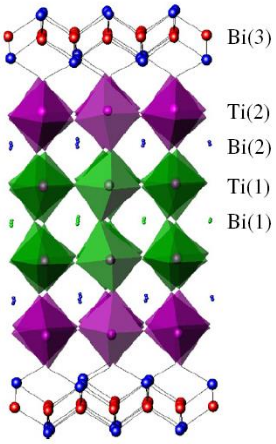

Figure 1. Representation of Arivillius $ABi_4Ti_4O_{15}$ (Ca, Sr, Ba) Oxide Structure (n = 4). Bi(1) and Bi(2) are in the perovskite layer, and Bi(2) is closer to the $[Bi_2O_2]^{2+}$ layer.

Aurivillius of $ABi_4Ti_4O_{15}$ (Ca, Sr, Ba) is atomically simulated at constant pressure using the GULP code. This simulation is based on lattice minimization, which is done iteratively. During this process, the forces on each ion are calculated. Then, the ion is shifted slightly in proportion to the forces acting on it. This process continues until the forces acting on all ions are zero. This study's simulation is determined by the Buckingham potential and the charge model (shell model) of the Aurivillius oxide. Potential Buckingham (short-range) and shell models (based on atomistic simulation results) suitable for Aurivillius $ABi_4Ti_4O_{15}$ oxide (Ca, Sr, Ba) are shown in Table 1.

The ease of polarized dopants can be determined by the shell's charge and the spring constant (polarizability). The shell charges of Sr and Ba are the same, but the spring constant is different, whereas Ca and Ba have the same spring constant, but the charge is different. The difference in the shell's charge or the spring constant shows that the ease of dopant ions is polarized (polarizability) also different.

Table 1. Buckingham potential (short-range) and shell model of ions from Aurivillius $ABi_4Ti_4O_{15}$ oxide (Ca, Sr, Ba)

a) *Short-range*	*A* (eV)	*r* (Å)	(eV Å^{-6})
$Bi^{3+}...O^{2-}$	49.529,35	0,2223	0,0
$Ca^{2+}...O^{2-}$	1186,6	0,2970	0,0
$Sr^{2+}...O^{2-}$	1956,702	0,3252	0,0
$Ba^{2+}...O^{2-}$	4818,416	0,3067	0,0
$O^{2-}...O^{2-}$	576,940	0,33236	0,0

b) *Shell model*		
Species	*k* (eV Å^{-2})	*Shell*(e)
Bi^{3+}	359,55	-5,51
Ti^{4+}	253,60	1,678
Ca^{2+}	34,05	1,281
Sr^{2+}	21,53	1,831
Ba^{2+}	34,0	1,831
O^{2-}	70,1512	-2,04

The simulation results show that the Sr> Ba> Ca polarizabilities, as shown in Figure 2. However, in theory, the smaller the ionic radius, the weaker the ionized is polarized by anions (oxygen), so the ease of the Ca, Sr, and Ba ions polarized oxygen is Ba> Sr> Ca. Differences in theoretical polarization and simulation results differ between Ba and Sr, where the simulation results show that Sr is more easily polarized than Ba. The phenomenon is caused by the weak bond between the nucleus of the atom and the electrons, as shown by the small Sr spring constant, 21 (eV Å^{-2}).

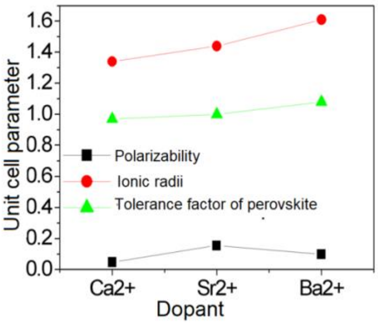

Figure 2. Polarizabilities, ionic radii, and perovskite tolerance factors of Aurivillius $ABi_4Ti_4O_{15}$ oxide (Ca, Sr, Ba).

The polarizability shows that the structure of $ABi_4Ti_4O_{15}$ experienced greater distortion compared to the Aurivillius $ABi_4Ti_4O_{15}$ (A = Ca, Ba). The cell parameters of *a* and *b* of $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) increased along with the increase in the concentration of dopants that partially substitute Bi both in Bi(1) and Bi (2) sites. On the other hand, the cell parameter *c* can either increase or decreases: Bi substitution by dopant in position Bi(1) decreases the value of *c* decreases, whereas substitution of Bi in Bi(2) increases the value of *c*. An exception to this rule is substitution with dopant Ca. The increase in the value of *c* is probably caused by the effect of repulsion of the pair of free electrons Bi, which is in t $[Bi_2O_2]^{2+}$ layer. Bi(2) is closer to the bismuth layer so that the repulsion of the electron pair to the ions in the site (2) of the perovskite layer is enormous. The easier the Sr and Ba ions polarized, the smaller the increase of the *a* and *b* values of the $ABi_4Ti_4O_{15}$ structure (A = Sr, Ba). However, the decrease in *c* value in $CaBi_4Ti_4O_{15}$ (Bi is substituted with Ca in Bi(2) site) is likely due to the fact that Ca ions, which are not easily polarized by oxygen.

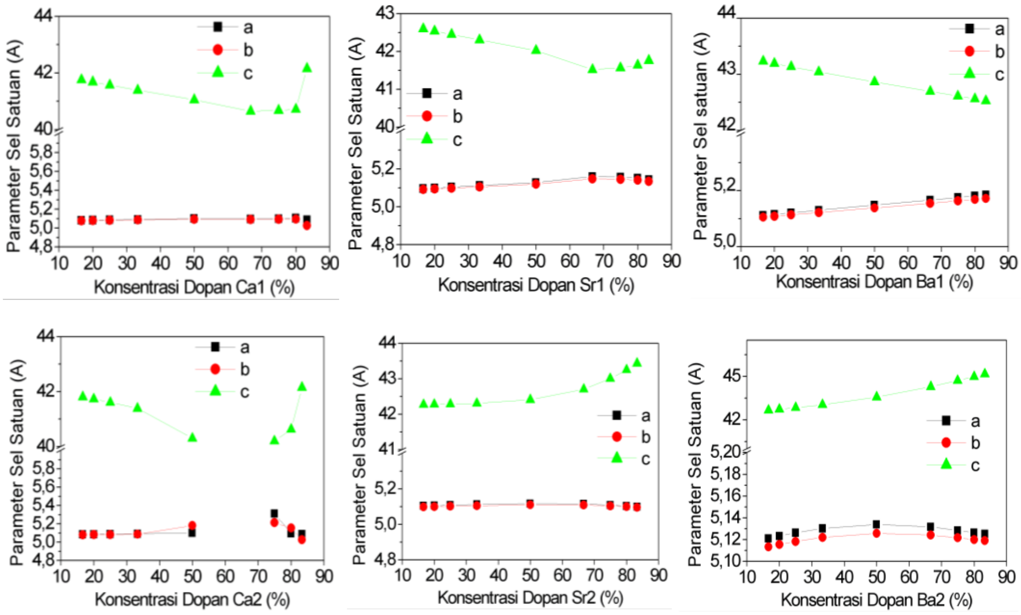

Figure 3. $ABi_4Ti_4O_{15}$ unit cell parameters (A = Ca, Sr, Ba); the values of a and b increase with increasing dopant concentration, but the value of c decreases when substituting in position Bi(1) and increases when substitution in position Bi(2).

The perovskite structure's stability can also be predicted by the tolerance factor of perovskite (*t*) proposed by Goldschmidt. This approach measures the size mismatch between cations A and B in the perovskite. The tolerance factor is defined as $t = (\langle r_A \rangle + r_O)/\sqrt{2}(r_{B+} r_O,$ where $\langle r_A \rangle$ is the average radius of cation A with dodecahedral coordination, r_B- ionic radius of cation B with 6-coordinate, r_O- oxygen radius of octahedral coordination [19]. The *t* value equals unity shows an ideal perovskite, while *t*<1 indicates a distorted perovskite system where tilt or rotation of the octahedral BO_6 is plausible. Among the dopants, Ba gives the highest level of distortion, with a tolerance factor far above those resulting in Ca and Sr. Sr's addition, which is almost the same as one has less slope than the other.

This result is different from the report of Reaney *et al.* (1994), who shows that perovskite at room temperature with 0.985<*t*<1.06 is expected to be undistorted. Perovskites with 0.964<*t*<0.985 typically have anti-phase slant structures, and perovskites with *t*<0.964 are expected to show phase-and anti-phase tilting [20], [21]. As *t* continues to decline, the stability of the perovskite system decreases and eventually destroys the structure. This observation is conceivable since the radius of the Shannon ion Bi^{3+} (r = 1.17 Å) is in 8-fold coordination, with *t* decreases to 0.8886 [22]. Therefore, the perovskite structure is not stable. However, if we consider that the Bi^{3+} ion is dodecahedral coordination with an ionic radius of 1.40 Å, then the *t* value indicates the distortion of BO_6 of $ABi_4Ti_4O_{15}$ doped with Ca^{2+}, Sr^{2+}, and Ba^{2+} to partially substitute Bi in the perovskite layer. An example was also observed in $BiFeO_3$ with a *t* value of 0.96 [23]–[25]. Thus the cation A size variance and tolerance factor (t) are also the factors responsible for the formation of perovskite octahedral distortion.

CONCLUSION

The unit cell parameters $ABi_4Ti_4O_{15}$ (A = Ca, Sr, Ba) fit well with the experimental unit cell parameters. The higher the dopant concentration, which substitutes Bi, then the bigger the Aurivillius $ABi_4Ti_4O_{15}$ lattice energy. $ABi_4Ti_4O_{15}$ is more stable when dopant (A) substitutes Bi in Bi(2) position with dopant concentration below 33%. Conversely, at a higher dopant concentration, the substitution of Bi by dopant A at position Bi(1) is more stable. The maximum limit of Ca dopants substituting Bi(2) is

33%, while other dopants can completely substitute Bi(2). This research can be used as a guide for the synthesis of Aurivillius $ABi_4Ti_4O_{15}$ compounds.

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