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CALCULATION OF PHONON PROPERTIES OF ASnI3 (A = Li, Na, OR Cs) PEROVSKITE IN CUBIC PHASE USING DENSITY FUNCTIONAL THEORY METHOD

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ABSTRACT

Perovskite solar cells utilize perovskite material as an active component to convert sunlight into electrical energy. Perovskite is a compound with the crystal structure ABX_3, where A and B are cations, while X is an anion, generally a halide. Research continues to find perovskite materials with high energy conversion efficiency. This efficiency is closely related to the phonon nature structure of the material, which is analyzed using the Density Functional Theory (DFT) approach. In this study, the phonon properties of $ASnI_3$ cubic perovskite (with A = Li, Na, and Cs) were analyzed using Quantum ESPRESSO software. Various parameters, such as cut-off energy, number of k-points, and lattice constant were optimized to obtain the most accurate results. The optimization results provided phonon density of states (PHDOS) curves, phonon dispersion curves, and dielectric constants for each of the three perovskite types. The phonon dispersion curves in this study explain that cubic $ASnI_3$ (with A = Li, Na, and Cs) is an unstable material because some of the wave functions in the material are at negative (imaginary) values. For the dielectric constant calculation, each of perovskite shows that $LiSnI_3$ is 24.22, $NaSnI_3$ is 6.18 and $CsSnI_3$ is 10.61, and LiSnI3 24.22, $NaSnI_3$ of 6.18 and $CsSnI_3$ of 10.61. By this fact, we argue that material LiSnI3 has the best potential to be component of perovskite solar cell if one shift it to orthorhombic phase based on Huang & Lambrecht (2014) research (Huang & Lambrecht, 2014).

Keywords: ASnI3, DFT, Quantum ESPRESSO, Phonon Dispersion, Dielectric Constant

INTRODUCTION

The law of conservation of energy states that energy cannot be created or destroyed, but it can change form. Energy is conserved meaning that the total amount of energy in a closed system remains constant. This law of conservation of energy makes scientists think about how to create energy that can be continuously replenished without causing too much negative impact on environmental sustainability. Energy is something that is abstract and difficult to prove, but its existence can be felt. One energy that is inexhaustible is solar energy (Purwoto, Jatmiko, Fadilah, & Huda, 2018).

Solar energy technology has advanced rapidly, one example being the innovation of DSSC (Dye Sensitized Solar Cell) developed by O'Regan and Grätzel in 1991. As part of the third generation of solar cells, DSSC offers a

number of advantages, such as low production costs, a simple manufacturing process, design flexibility, and good efficiency. These advantages make it a promising alternative to silicon-based solar cells. Over time, the appeal of DSSC has driven an increase in power conversion efficiency (PCE) from 7.1% to 14.7% (Nursam & Oktaviana, 2020).

The latest generation of solar cells, which are the result of developments in Dye-Sensitized Solar Cells (DSSC), are perovskite solar cells (PSC). In recent years, PSCs have achieved a PCE of up to 23.3%. Hybrid perovskite halides are compounds composed of organic and inorganic components with the general formula ABX_3 (Wardana, 2022), where in this paper, A represents lithium (Li), Natrium (Na), Cesium (Cs), B represents tin (Sn), and X represents an Iodine (I).

Hasan et al. (2024) have calculated the electronic, optical, and mechanical properties for LiSnI3 and NaSnI3 perovskites using CASTEP software. They discovered that the perovskite undergo phase transitions from semiconductor behavior to metallic behavior (Hasan, Apon, Ovi, & Zahra, 2024). Regarding about CsSnI3, recent reports showed that it has band gap energy 1.019 eV (Azhar, Aliah, & Pitriana, 2023) and unstable characteristic (Rahmani, Aliah, & Pitriana, 2023). It is important to note that all of the preceding results are done in cubic phase.

Motivated by Rahmani et al. (2023) work, we carry out the calculation for phonon properties which have never been done for LiSnI3 and NaSnI3 until presently based on our knowledge. The calculation method known as Density Functional Theory (DFT) was first developed by Hohenberg and Kohn through two theorems that explain the relationship between electron density and electron-electron interactions. Subsequently, Kohn, together with Sham, refined this method by formulating the Kohn-Sham equation as the primary basis for the application of DFT (Sidik, 2022). There are no analytical solution to DFT so numerous DFT software packages, such as Quantum ESPRESSO (QE), have been created to solve it numerically (Rademaker, 2020).

To obtain information about the phonon properties of AsnI3 (A = Li, Na, or Cs), we use the QE software because it is an open source code (Giannozzi et al., 2009). Researchers initially must first identify the most appropriate calculation parameters. The parameters in question include ecutwfc (energy cutoff), k-Points, and lattice constants. These values are then used by the software to identify the phonon characteristics of the perovskite.

RESEARCH METHOD

Research Tools

The tools used in this study consisted of software and hardware. The software includes VirtualBox, Quantum ESPRESSO, Visualization for Electronic and Structural Analysis (VESTA), gnuplot, Notepad++, and Adobe Photoshop CS3, while the hardware consists of a laptop with an Intel(R) Core(TM) i3-6006U CPU @ 2.4GHz 1.99 GHz processor and 8.00 GB RAM (3.88 GB usable).

Material Modelling

Before running scf, ph, q2r, and matdyn calculation, we modeled the researched crystal structure using VESTA in figure 1. As an example, we visualized perovskite LiSnI3 in cubic phase. This crystal structure has the most optimum lattice constant which has been optimized through vc-relax calculation (see lattice constant optimization part). This issue is very important to verify that our structure is whether optimum or not.

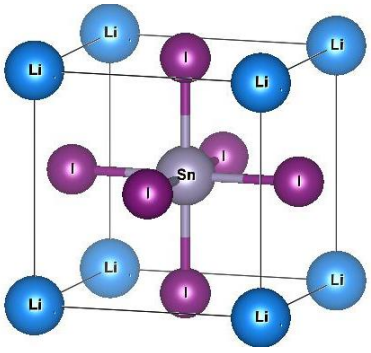


Figure 1. LiSnI3 Crystal Structure in Cubic Phase. (Blue: Li; Purple: I; Gray: Sn)

Calculation Parameters

Structural calculations were performed using the GGA-PBE exchange-correlation functional. The minimum value of ecutwfc was determined based on information from pseudopotential data, where the type of pseudopotential used was Semi Local Norm Conserving with Generalized Gradient Approximation Perdew Burke Enzerhof Exchange correlation functional (GGA-PBE). To obtain accurate phonon property calculations for ASnI3 materials (A = Li, Na, or Cs), optimization of several important parameters is required, namely ecutwfc, k-points, and lattice constant.

RESULT AND DISCUSSION

Convergence of Ecutwfc and K-points

The results of ecutwfc parameter optimization for LiSnI3 calculations in the range of 10–110 rydberg are shown in Figure 2. From 50 to 110 rydberg, the total energy value does not change significantly. Therefore, 90 rydberg was chosen as ecutwfc because the researcher took 4 decimal places. Using the same method, the values obtained for perovskite $NaSnI_3$ are 90 Ry, and for $CsSnI_3$ are 80 Ry. As is known, the larger the cutoff energy value, the more precise the calculation becomes, but the time required also increases.

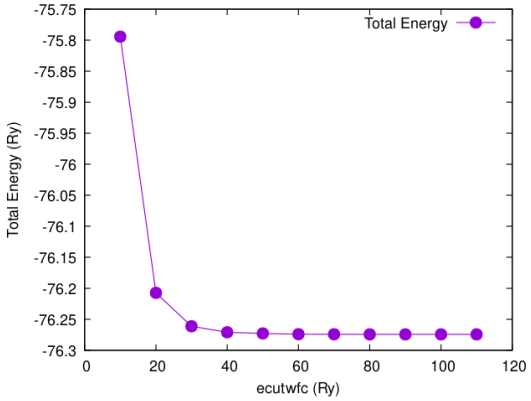


Figure 2. Ecutwfc Convergence Chart

The optimal k-points values are determined by inputting random numbers while ensuring that the sequence of numbers represents the ground k-points positions. The crystal structure used is cubic, while k-points have a general formula, namely n x n x n. Therefore, to determine the optimal k-points values, random numbers are input starting from 1 x 1 x 1 (Wahyuni, 2022).

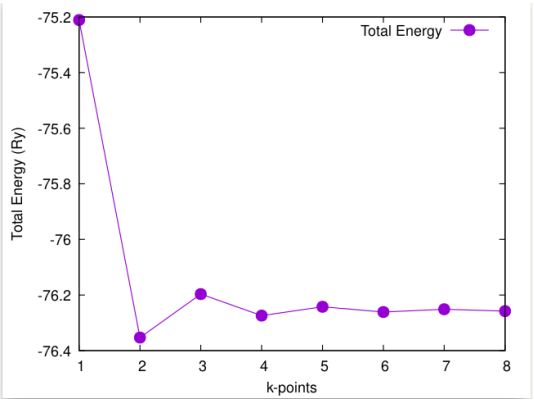


Figure 3. K-Points Convergence Chart

Figure 3 shows the comparison of k-points with total energy for LiSnI3. From the values 6 x 6 x 6 to 8 x 8 x 8, the total energy values do not change significantly. Therefore, the value 7 x 7 x 7 was selected as the k-points because the researchers took two decimal places. Using the same method, the k-points for perovskite $NaSnI_3$ 6×6×6 and k-points for $CsSnI_3$ 6×6×6 were obtained. Meanwhile, for perovskite $NaSnI_3$ and $CsSnI_3$, the total energy oscillates around the convergent value (Hung, Nugraha, & Saito, 2023) As is well known, the higher the k-points value, the more accurate the calculation will be, but the longer the time required (Shanaz, 2019).

Lattice Constant Optimization

The results of the calculation (comparison) of the lattice constant values of the LiSnl3 lattice constant value can be seen in Table 1:

Table 1. Calculation results of the LiSnl3 lattice constant value

$a_{initials}$ (Å)	$a_{relaxation}$ (Å)	Total Energy (eV)
5	6.180	-76.2355
6.180	6.181	-76.7862
6.181	6.181	-76.7861

Table 2. Comparison of Lattice Constants

Lattice Constant Calculation (Å)	Lattice Constant (Å) Reference	Percentage Error
6.181	6.175 (Sagala, Sirait, & Ong, 2024)	0.09 %

6.181	6.206 (Hasan et al., 2024)	0.40 %

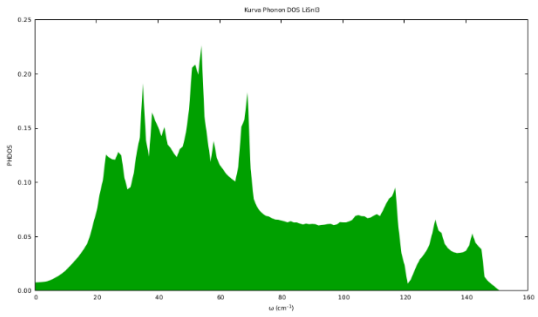
The initial lattice constant is set to 5 Å. After performing the vc-relax calculation, the lattice constant will increase until the optimal lattice constant is obtained. When the optimal lattice constant value is entered into the next input file, the total energy value does not change. This is due to the shift in the lattice parameter values set as initial estimates in the SCF input to the optimized values after the program is run (Maysari Angraini, Gusti Ngurah Yudi Handayana, & Wayan Sudiarta, 2021). We only showed the relaxation for LiSnI3 as shown in table 1. To guarantee the result, we compare our result with two references which yield low error percentage. Subsequently, for the perovskite $NaSnI_3$, it is 6.185 Å and for the perovskite $CsSnI_3$, it is 6.199 Å.

From the table 2, it can be concluded that the calculated lattice constant and the reference lattice constant have values that are not significantly different, as can be seen from the small percentage error.

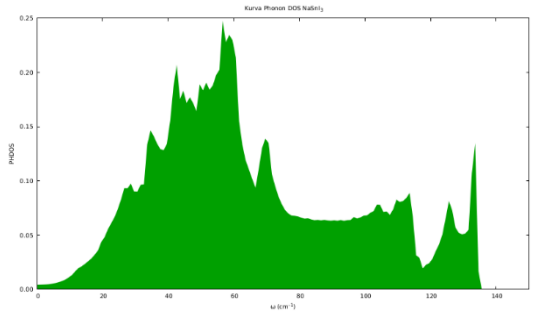
Phonon Density Of States (PHDOS) curve

The PHDOS curves for ASnI3 perovskites (A = Li, Na, or Cs) are shown in Figure 4:

(a) LiSnI3



(b) NaSnI3



(c) CsSnI3

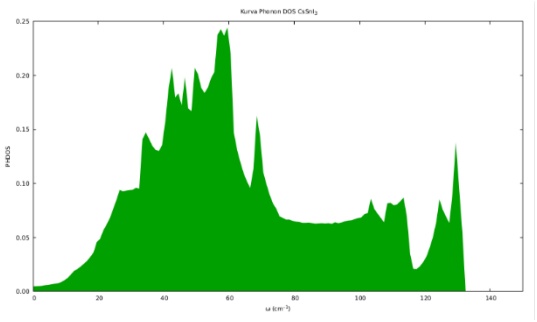


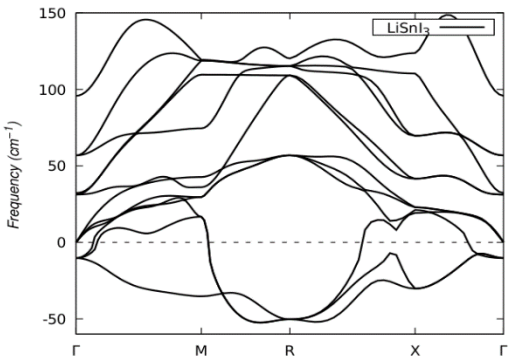
Figure 4. Phonon Density Functional Theory curves for perovskites (a) LiSnI3, (b) NaSnI3, (c) CsSnI3.

The phonon density of states calculation uses the results of the previous optimization. PHDOS covers the range from zero to the maximum phonon frequency present in a particular crystal. PHDOS describes the distribution of phonons at each frequency. In the PHDOS wave function curve above, it can be seen that the maximum phonon distribution in LiSnI3 perovskite occurs at a wave frequency of 52.04 cm-1; NaSnI3 perovskite is at a wave frequency of 56.62 cm-1; and CsSnI3 is at a wave frequency of 59.52 cm-1, as shown in Figure 4.

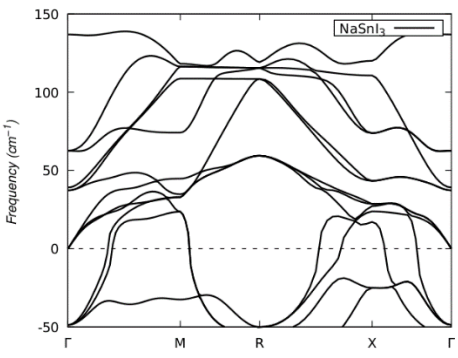
Fonon Dispersion Curve

The fonon dispersion curve results for ASnI3 perovskite (A = Li, Na, or Cs) can be seen in Figure 5:

(a) LiSnI3



(b) NaSnI3



(c) CsSnI3

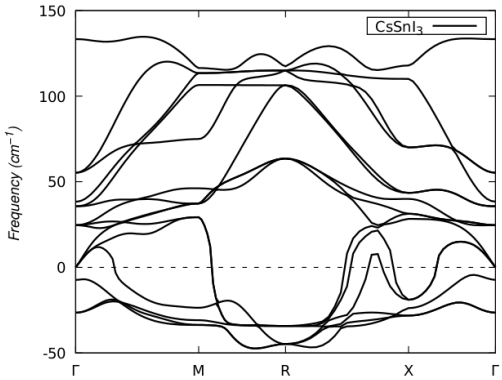


Figure 5. Fonon dispersion curves of perovskite (a) LiSnI3, (b)NaSnI3, (c) CsSnI3.

The phonon dispersion curve in Figure 5 shows the relationship between wave frequency and k-points in inorganic perovskite. In the phonon dispersion curve above, we can see the distribution of wave frequencies at each k-points. The k-points used in CsSnI3 are limited to the gamma point, so not all phonon wave frequencies at the k-points are shown in the curve above. Since CsSnI3 has 5 atoms (1 Cs atom, 1 Sn atom, and 3 I atoms), there are 15 wave frequencies in the phonon dispersion curve. Figure 5 display 15 curves representing each atom in each perovskite. From the phonon dispersion curve for the inorganic perovskite $ASnI_3$ (A = Li, Na, or Cs) above, it can be seen that there are some frequencies on the negative (imaginary) side. In reality, there are no negative frequencies, but since this is done computationally, the imaginary part of the frequency (ω<0) is considered negative. Since there are several frequencies with negative (imaginary) values, it can be concluded that $ASnI_3$ (A = Li, Na, or Cs) is a phonon-less stable perovskite. The instability of perovskite in CsSnI3 is supported by previous researchers who used CsSnX3 (X=CL, Br, I) as the base material for solar cells by adding CsSnI3 molecules to form a new molecule, Cs2SnI6, resulting in a more stable molecule (Qiu et al., 2017).

Dielectric Constants

Table 3. Comparison of Dielectric Constans

Dieletric Constant	Dielectric Constant Reference	Percentage Error
24.22 ($LiSnI_3$)	-	-
6.18 ($NaSnI_3$)	-	-
6.03 ($CsSnI_3$)	7.2 (Wang, Tal, Bischoff, Gono, & Pasquarello, 2022)	16 %

The table above only compare CsSnI3 result since there is no available dielectic constant for NaSnI3 and LiSnI3 based on author knowledge. One can see that the percentage error is large enough because the reference's phase is in orthorhombic phase. The orthorhombic phase research will be considered as the future work. By the definition of dielectric constant, the highest dielectric cosntant, LiSnI3, is the best perovskite material. One may shift it to the orthorhombic phase to make it stable since these phase did not exhibit any negative (imaginary) frequency in their phonon dispersion curve (Huang & Lambrecht, 2014).

CONCLUSION AND SUGGESTION

From the calculations performed, it can be concluded that the phonon dispersion curves for the $LiSnI_3$, $NaSnI_3$, and $CsSnI_3$ perovskites contain negative (imaginary) phonon wave frequencies in the cubic phase. These negative frequency values indicate that the three perovskites in the cubic structure are dynamically unstable. Then, we calculate the dielectric constant to determine the best perovskite. The dielectric constant to perovskites LiSnI3, NaSnI3, and CsSnI3 are 24.22, 6.18, and 6.03 respectively. By the proof from Huang & Lambrecht (2014) research, we argue that the best perovskite is LiSnI3 in since it has the best performance when its orthorhombic phase used as the component of perovskite solar cell (Huang & Lambrecht, 2014).

Suggestions for future researchers to explore thermal properties for the same

perovskite, as well as varying the orthorhombic phase or other phases.

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