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A DFT STUDY ON THE PHONON PROPERTIES OF PEROVSKITES $ASnCl_3$ (A = K, Rb, AND Cs)

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ABSTRACT

Inorganic perovskites such as $ASnCl_3$ (A = K, Rb, and Cs) are widely used in solar cells because they are known to have many advantages, such as being easily obtainable and having high efficiency. Therefore, in this study, we conducted computational study to determine the phonon properties of $ASnCl_3$ perovskites (A = K, Rb, and Cl) with a pm3m space group in a bulk system. These properties were calculated using density functional theory (DFT) through the Quantum ESPRESSO program. The phonon properties discussed are phonon density of states (PHDOS) and phonon dispersion. In addition, the dielectric constant was also calculated because the code is straightfoward in the dynamical matrix process. To calculate the phonon properties, the optimum lattice constant must be achieved through k-point optimization and kinetic energy cut-off. The results show that the highest phonon distribution in $KSnCl_3$, $RbSnCl_3$, and $ClSnCl_3$ perovskites is at frequencies of -68.52 cm^{-1}, -55.37 cm^{-1}, and 55.83 cm^{-1}, respectively. The presence of phonon distribution or phonon dispersion curves at negative frequencies explains that $ASnCl_3$ perovskites (A = K, Rb, and Cl) are unstable perovskites. Nevertheless, the dielectric constants of these three perovskites are quite good, making them very promising as active materials for perovskite solar cells. When compared to the reference static dielectric constants, the obtained values are consistent with the Lyddane–Sachs–Teller relation

Keywords: $ASnCl_3$ (A = K, Rb, and Cs), DFT, phonon dispersion, PHDOS

INTRODUCTION

It makes sense to use solar energy as a source of energy because the sun is a limitless supply of energy. Utilizing solar energy as a source of energy promotes the quick development of solar cells, leading to the emergence of numerous novel varieties. Due to their numerous benefits, materials with perovskite structures are now being extensively studied for use in a variety of fields, including enhancing the environmental stability and power conversion efficiency (PCE) of perovskite solar cells (PSCs) (S. Wang et al., 2021) and developing flourescent sensors based on lead-based perovskite nanomaterials (G. Huang et al., 2021).

The material known as perovskite, which possesses the same crystal structure as $CaTiO_3$, was initially found in the Russian Ural Mountains in 1839 by Gustav Rose and was named for the Russian mineralogist L.A. Perovski (Katz, 2020). The general chemical

formula for a perovskite compound is ABX_3, in which X is an anion that forms a bond with both cations and 'A' and 'B' are two cations of different sizes (Brittman, Adhyaksa, & Garnett, 2015).

In 2018, the use of perovskite-type methylammonium lead iodide ($MAPbI_3$) achieved a maximum light conversion efficiency of 23.7%. However, this perovskite experienced chemical instability due to the volatile and hygroscopic properties of organic cations at high temperatures. Therefore, inorganic metal halide (IMH) perovskite emerged as a promising alternative with superior stability and comparable properties (Swarnkar et al., 2016).

There are many recent studies regarding with this type of perovskite through computational method. For example, materials which have been researched are $ASnX_3$ (A = Rb, K; X = Cl, Br) (Khan, Sahariya, & Soni, 2021), $CsSnX_3$ (X = Cl, Br, I) (Rahmani, Aliah, & Pitriana, 2023), $RbSnX_3$ (X = F, Cl, and Br) (Kumari, Sharma, Lilhore, Khenata, & Srivastava, 2022) , and $ASnI_3$ (A = K, Rb, and Cs) (Gul et al., 2023). In general, theirs structural, electronic, optical, phonon, thermoelectric, and mechanical properties are to be determined. Some researchers like to redone one's work with the other phases while maintaining the same material (the same chemical formula).

Based on the recent works development, this study aims to find out the stability of inorganic $ASnCl_3$ (A = K, Rb, and Cs) perovskite in cubic phase from the perspective of phonon characteristics. $RbSnCl_3$ and $KSnCl_3$ are chosen because their phonon properties have never been studied before, while $CsSnCl_3$ is chosen to be compare with reference later. Two different kinds of curves—phonon dispersion and phonon density of states (PHDOS)—are the outcome of this investigation. The maximum phonon distribution, which indicates the amount of phonon in each frequency, may be calculated from the PHDOS curve (Bassani, Liedl, & Wyder, 2005). One may conclude the material is mechanically If the PHDOS or phonon dispersion curve does not appear at all in the negative frequency zone (Parlinski & Kawazoe, 2000).

To obtain information about the phonon properties of $ASnCl_3$ (A = K, Rb, and Cs), we apply the firs principle method through Quantum ESPRESSO (QE) software because it is an open source code (Giannozzi et al., 2009). The most important parameter to be found by any researchers are the optimum lattice constant. In spite of the same phase, one cannot pick it up directly from any experimental value. This optimum value are then typed inside the scf code.

RESEARCH METHOD

Research Tools

QE was the software to calculate the phonon structure of inorganic perovskite $ASnCl_3$ (A = K, Rb, and Cs) based on the density functional theory (DFT) approach. The crystal structure were simulated by VESTA (shown in figure 1). The input script code for QE/VESTA were typed in notepad++ software. Finally, any graph were drawn by gnuplot, while Adobe photoshop is used to edit figure so that it will be easy to read and understand by reader.

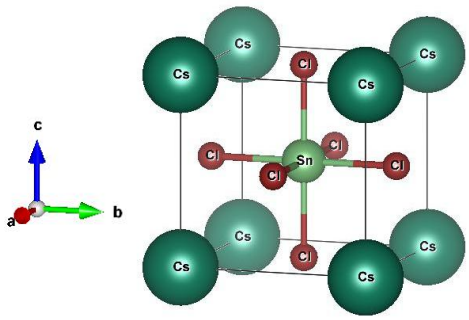


Figure 1. $CsSnCl_3$ Crystal Structure in Cubic Phase. (Hunter Green: Cs; Pistachio: Sn; Brown: Cl)

The calculation is split into two phases: obtaining the optimum cut-off energy (ecutwfc), **k**-points, and lattice constant and determining the phonon structure that is phonon dispersion and PHDOS. Besides that, we also calculate the high-frequency dielectric constant (or usually called electric constant [ε_∞]) which is straightforward while creating the dynamical matrix calculation script code. All of these calculation used Troullier–Martins

norm-conserving pseudopotential with generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional.

RESULT AND DISCUSSION

Convergence of Ecutwfc and K-points

In general, the ecutwfc parameter is the first parameter to be determined. To obtain the optimal ecutwfc value, we input increasing variations of ecutwfc with a specific pattern. Researchers start from ecutwfc = 10 Ry to 110 Ry with an increase of 10 Ry. This variation pattern is applied to each perovskite studied, namely KsnCl3, RbSnCl3, and CsSnCl3. The total energy versus ecutwfc graph for KSnCl3 perovskite is represented in Figure 2.

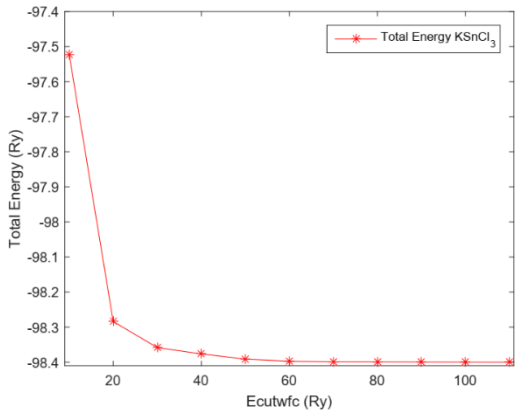


Figure 2. Ecutwfc Convergence Chart for KSnCl3 Perovskite

Based on the numerical value of figure 2, it can be seen that the total energy of each perovskite converges when ecutwfc = 70 Ry. However, we chose ecutwfc = 90 Ry as the optimal value because the convergence of total energy is limited to 3 decimal places. This limit was chosen because the higher the ecutwfc selected, the longer the scf calculation process will take. If this is applied, the subsequent calculations (vc-relax, PHDOS, and phonon frequencies) will take a very long time. The most important point is that the selected ecutwfc value exceeds the minimum ecutwfc value recommended by the pseudopotential data for each atom (Hung, Nugraha, and Saito, 2023). By mimicing the same step and reason as KSnCl3, ecutwfc = 90 Ry is also chosen for RbSnCl3 and CsSnCl3 perovskites.

The k-points parameter is the second parameter determined after ecuwfc. To obtain the optimal k-points value, researchers input random k-points variations with a specific pattern. According to Wahyuni, et al. (2022), the general formula for k-points is n x n x n, so the determination of k-points starts from a 1 x 1 x 1 grid. The SCF calculation was limited by the researchers to a 10 x 10 x 10 grid with an increment of 1 for each k-point. The total energy versus ecutwfc graph for KSnCl3 perovskite is represented in Figure 3.

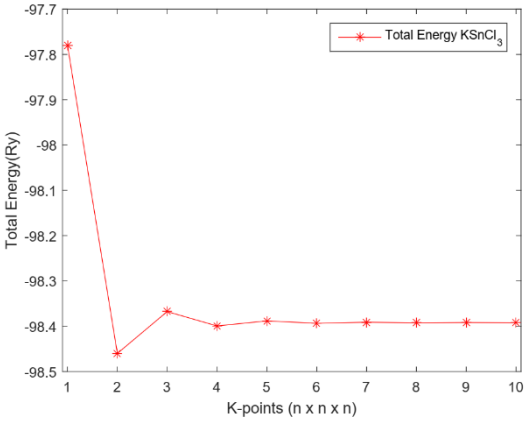


Figure 3. K-Points Convergence Chart for KSnCl3 Perovskite

Based on figure 3, we selected 6 x 6 x 6 grid. Such k-points parameter were chosen because at those grid k-points, the total energy values began to converge oscillatory (see Figure 3). Due to the natural symmetry of the cubic structure, QE was allowed to shift half the distance between grids in all directions (x, y, and z). The reason for selecting these k-point sizes was based on the QE calculation time for total energy. A high grid size would cause programming time inefficiency, even though the results would be more accurate. If one continued with this, the subsequent calculations (vc-relax, PHDOS, and phonon frequencies) would take a very long time. By mimicing the same step and reason as KSnCl, 8 x 8 x 8 grid is chosen for RbSnCl3 perovskite, while 7 x 7 x 7 grid is chosen for CsSnCl3 perovskite.

Lattice Constant Optimization

The lattice constant value (arelaxation) obtained from the computation are displayed in Table 1 alongside with its initial value (ainitial). As can be shown, the second calculation, which uses ainitial = 5.543 Å did not change anymore after vc-relax calculation. Thus, this value is considered as the most ideal lattice constant for KSnCl3 crystal structure. A similar procedure was also applied to the RbSnCl3 and CsSnCl3 perovskites. It can be seen that all optimum lattice constants have nearly the same value of around 5.54 Å.

Table 1. Calculation results of the KSnCl3 lattice constant value

$a_{initial}$ (Å)	$a_{relaxation}$ (Å)	Total Energy (eV)
5	5.543	-98.502
5.543	5.543	-98.502

Table 2. Calculation results of the KSnCl3 lattice constant value

A Kation	$a_{relaxation}$ (Å)	Total Energy (eV)
Rb	5.546	-98.458
Cs	5.544	-98.440

Evidence of the accuracy of the lattice constant values obtained by us are shown through comparison with the references in Table 3. Each error percentage is less than 1% between the results of this study and the results of other computational studies. These indicate that our results are scientifically acceptable.

Table 3. Comparison of Lattice Constants

Perovskit	Lattice Constant (Å) Reference	Percentage Error
$KSnCl_3$	5.596 (Khan et al., 2021)	0.947
$RbSnCl_3$	5.558 (Kumari et al., 2022)	0.216
$CsSnCl_3$	5.4901(Hayatul lah et al., 2013)	0.964

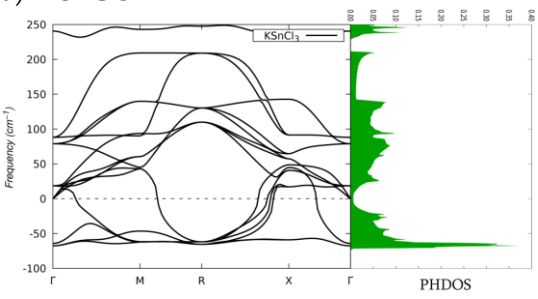
Clinical Applications of MIP/SIP Biosensors for Infectious Diseases

The emergence of differences when reviewed to three decimal places may be due to differences in the values of ecutwfc, k-points, and lattice constant or the used exchange-correlation functional type and pseudopotential type. For example, $KSnCl_3$ perovskite has an error percentage of 3%. This is because Khan (2021) used the Wien2k program code and the Tran-Blaha modified Becke-Johnson (TB-mBJ) approximation as the exchange-correlation potential. If any previous studies/recent researchers use the QE program with the same exchange-correlation functional type and pseudopotential type, the relaxation lattice constant value will definitely be the same (5.543 Å). We did not compare with experimental reference values because we focused on phonon properties.

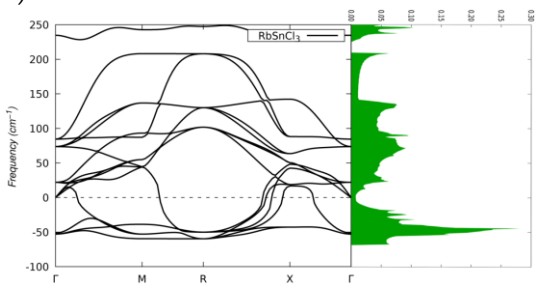
Phonon Dispersion curve And PHDOS Curve

According to Parlinski and Kawazoe (2000), the phonon dispersion graph aims to show the phonon frequency at a specific k-point. Through this graph, one can determine whether a particular material is stable or not. A material is said to be stable if all phonon frequencies are positive and conversely, it is said to be unstable if there are phonon frequencies that are negative (there are certain curves below zero) (Parlinski & Kawazoe, 2000). The phonon dispersion curve and PHDOS curves for $ASnCl_3$ (A = K, Rb, and Cs) perovskites are shown in Figure 4 as following:

a) KSnCl3



b) $RbSnCl_3$



c) $CsSnCl_3$

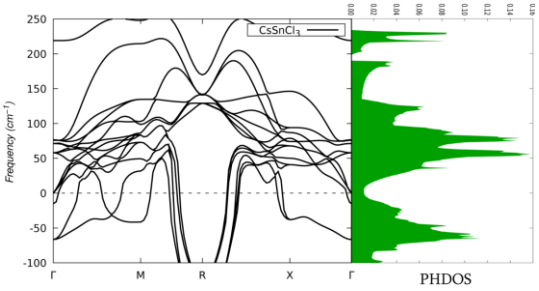


Figure 4. Phonon Dispersion Curve (left) and PHDOS curves for perovskites (a) $KSnCl_3$, (b) $RbSnCl_3$, (c) $CsSnCl_3$.

Phonon Dispersion Graphs show the distribution of wave frequencies at each k-point. The k-points used refer to Rahmani et al. (2021) paper, namely the Γ, M, R, X, and Γ points (Rahmani et al., 2023). Focus on $CsSnCl_3$ result (Figure 4. (c)), there is a significant difference between ours and theirs. This may be due to the difference in the pseudopotential used, where they used the Projected Augmented Wave (PAW) method. The main reason for this difference should be the use of lattice constant values, which the author directly quoted from Hayatullah et al. (2013) (Hayatullah et al., 2013). This is not accepted in determining DFT research because there will always a small difference between numerical and experimental result. According to the chemical formula, $ASnCl_3$ (A = K, Rb, or Cs) has 5 atoms, so there will be 15 wave frequencies (15 curves) on the phonon dispersion graph.

Although the $CsSnCl_3$ phonon dispersion curve obtained by us with reference is different, there is still have one thing in common, namely the discovery of several frequencies with negative (imaginary) values, making $CsSnCl_3$ an unstable material. A material is said to be stable if there are no wave frequencies with negative values at all. For example, the $CsSnCl_3$ monoclinal phase phonon dispersion graph simulated by Huang and Lambrecht (2013) (L. Huang & Lambrecht, 2014). Based on this $CsSnCl_3$ evidence, if the $KSnCl_3$/$RbSnCl_3$ material shift to orthorhombic/monoclinal phase, it is likely that they will also be stable. This hypothesis will be a future work for us.

PHDOS is defined in exactly the same way as density of states (DOS), namely the number of phonon modes per volume per frequency. PHDOS ranges from zero to the maximum phonon frequency value in a crystal (Z. Wang, Cheng, Zhou, Liu, & Zhou, 2021). In the right path of figure 4, it can be seen that the maximum phonon distribution for $KSnCl_3$, $RbSnCl_3$, and $CsSnCl_3$ materials are at wave frequencies of -68.52 cm^{-1}, -55.37 cm^{-1}, and 55.83 cm^{-1}, respectively. The highest PHDOS values at these wave frequencies indicate that the most phonons are scattered at these frequencies. The presence of PHDOS at negative frequencies indicates the instability of those crystal structures.

Dielectric Constants

The dielectric constant calculated from the module ph.x is shown in Table 4.5. Till the best of the recent knowledge, the experimental value of ε_∞ for $ASnCl_3$ perovskite (A = K, Rb, or Cs) is not currently available, so the static dielectric constant (ε_0) is presented from the reference to connect both through the following explanation

Table 4. Comparison of Dielectric Constans

Perovskit	Calculate Dielectric Constant	Static Dielectric Constant
$KSnCl_3$	4.276	3,39 (Khan et al., 2021)
$RbSnCl_3$	4.662	3,44 (Khan et al., 2021)
$CsSnCl_3$	5.855	4,14 (Hayatullah et al., 2013)

The dielectric constant results in Table 4.4 can be justified through the Lyddane–Sachs–Teller relation as follows:

$$\varepsilon_\infty = \frac{\omega_l^2}{\omega_t^2}\varepsilon_0 \qquad (1)$$

Where is ω_l = transverse optical phonon frequency, while ω_t = longitudinal optical phonon frequency. Both frequencies can be observed experimentally through infrared absorption, transmission, or reflection experiments (infrared activity) or through scattering experiments (Raman activity). It should also be noted that these two frequency characteristics only exist for solid vibrations that require light (Kittel, 2005). If one considers equation (1), $\varepsilon_\infty \propto \varepsilon_0$, so that when $\varepsilon_0$increases, ε_∞ must also increase. This fact is consistent with the our computational results, where the high-frequency dielectric constant increases propotionally with the increase of the static dielectric constant (cation A: K—Cs).

CONCLUSION AND SUGGESTION

Conclusion

From the phonon dispersion curve or PHDOS curve, it can be concluded $KSnCl_3$, $RbSnCl_3$, and $CsSnCl_3$ perovskites contain negative (imaginary) phonon wave frequencies in the cubic phase. These negative frequency values indicate that those three perovskites is a a less stable material. However, the dielectric constant values show that they are potential to be the material for perovskite solar cell. Besides, our results consistent with Lyddane–Sachs–Teller relation.

Suggestion

Suggestions for future researchers to explore phonon properties for the same perovskite but in orthorhombic phase or monoclinic phase. It is strongly suspected that they will not be found any soft phonon modes based on Huang and Lambrecht paper (2014).

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