Journal of Minerals and Materials Characterization and Engineering, 2024, 12, 237-246
https://www.scirp.org/journal/jmmce
ISSN Online: 2327-4085
ISSN Print: 2327-4077

The Effect of External Pressure on Mechanical Properties of Aquamarine Gemstone Using First Principles Studies

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How to cite this paper: Kahuluda, E., Rao, P.V.K. and Mwanga, S. (2024) The Effect of External Pressure on Mechanical Properties of Aquamarine Gemstone Using First Principles Studies. *Journal of Minerals and Materials Characterization and Engineering*, **12**, 237-246.
https://doi.org/10.4236/jmmce.2024.125015

Received: May 17, 2024
Accepted: August 23, 2024
Published: August 26, 2024

Abstract

Aquamarine gemstones are popular jewelry in the gemstone trade and are currently one of the important products in the world market because of their economic value. Aquamarine is a Beryllium Aluminium Silicate with the chemical formula $Be_3Al_2Si_6O_{18}$ and crystallizes in the hexagonal system with space group P6/mcc (192), and Tanzania has wide deposits of aquamarine gemstones. The quality of gemstone depends on its characteristic properties, including electronic, optical, and mechanical properties. In the present study, the effect of external pressure on mechanical properties including independent elastic constants and other related parameters such as Bulk modulus, Shear modulus, Young modulus, Poisson's ratio, and Compressibility were studied. Density Function Theory in the forcite module of the material studies software on the external pressure within the range of 0 - 200 GPa on the optimized structure at electrostatic, Van der Waals and Ewald terms were used in this study. The results reveal that the independent elastic constants are mechanically unstable at 50 - 120 Gpa and are stable at 0 - 40 GPa and above 120 GPa, with the average bulk modulus, shear modulus, young modulus, Poisson's ratio of 2319.9447, 652.3058, 1789.2236, and 0.26 respectively with the compressibility of 0.059921/TPa, this indicates that aquamarine gemstones are stable against strain and strongly against shear stress but opposing shear deformation. These values are within other crystalline materials found in the literature. This provides technological backing for the comprehensive valuation of mechanical properties, quality, and stability of gemstones available in Tanzania.

Keywords

Aquamarine Gemstones, Mechanical Properties, External Pressure, Biovia Material Studio, Forcite Module

1. Introduction

Information shows that aquamarine gemstones are currently one of the Tanzania gemstones products it her market because of their economic value [1]. This gemstone is a Beryllium Aluminium Silicate with the chemical formula $Be_3Al_2Si_6O_{18}$ and exhibits a hexagonal structure with P6/mcc (192) space group [2] [3]. Most aquamarine gemstone is found in the Namtumbo district, Ruvuma region [1].

Researchers have studied various properties of the gemstone experimentally and theoretically and observed that its colors vary from light blue to greenish blue with other possible variants as shown in **Figure 1** and **Figure 2** [4]. Further, the study revealed that gemstone hardness values vary from 7.5 - 8.0, specific gravity between 2.67 - 2.71, and refractive index between 1.577 - 1.583 [5]. However, many properties such as mechanical, optical, and electronic properties still need to be explored because the quality of a gemstone depends widely on the nature of the mineral and its origin and external pressure due to the height from sea level [6] [7].

Figure 1. Beryl varieties [4].

Figure 2. Aquamarine raw stone [4].

Understanding elastic constants and elastic moduli is crucial to knowing the mechanical characteristics of materials [8]. To obtain important information on the stability unit cell structure by calculating the elastic constant and the elastic modulus such as bulk modulus *B*, shear modulus *G*, Young's modulus *E*, and Poisson's ration are important to be known to establish the stability of the crystal

[9]. Each material has certain respect of strengths and weaknesses in certain respect [10].

Density Functional Theory (DFT) is the most widely used *ab initio* quantum computational framework for theoretically understanding the material properties at the atomistic level [11]. DFT calculations utilized the total energy and plane-wave methodology to solve the Kohn-Sham equation [9], and investigate mechanical properties of the materials [12]. The mechanical properties of the crystal's stability are due to its capacity to withstand external stress and can be studied by elastic properties [13]. This study intends to investigate and analyze the mechanical properties of aquamarine gemstones using the DFT method to explore their mechanical properties at the atomistic level under applied external pressure in the range of 0 - 200 GPa.

2. Methodology

The crystal structure was built in the materials studio software package from the experimental values of the crystal system obtained from the crystalline database [14]. The geometry optimization of the structure was carried out using the forcite module [15]-[17]. During optimization and energy calculations, a smart algorithm with universal force fields was used, with an ultra-fine quality setting of 2×10^{-5} kcal/mol of energy, 0.001 kcal/mol/Å of force, and 1×10^{-5} Å of displacement [18]-[20].

After the geometry optimization of the structure, the mechanical properties were computed on the geometry optimization results obtained using the forcite module [16] [19]. During these calculations, the stiffness constants Cijs were first calculated using the elastic matric Equation (1) [21]. Independent elastic constants C_{11}, C_{12}, C_{44} and C_{66} obtained from the results of the stiffness matrix C_{ij} independently for all external pressure were used to analyze the necessary stability criteria are presented on Equation (2) [8] [9] [22] [23].

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & \\ & C_{11} & C_{13} & \\ & & & C_{33} \\ & & & C_{44} \end{pmatrix} \tag{1}$$

$$\begin{gathered} C_{11} > \left|C_{12}\right| \\ 2C_{13}^2 < C_{22}\left(C_{11} + C_{12}\right) \\ C_{44} > 0 \end{gathered} \tag{2}$$

Similarly, Bulk modulus (B) and shear modulus (G) were calculated from Reus, Voight, and Hill using Equations (3) and (4), while Youngs' Modulus and Poisson's ratio were calculated by using Equations (5) and (6) respectively as used elsewhere [23]-[27].

$$B = \frac{BV - BR}{2} \tag{3}$$

$$G = \frac{GV + GR}{2} \tag{4}$$

where: BV is the Bulk Modulus Voigt,

BR is the Bulk modulus, Reus,

GV is the Bulk Modulus Voigt,

GR is shear modulus Reus,

$$Y = \frac{9BG}{3BG + G} \tag{5}$$

$$v = \frac{3B - 2G}{2(3B + G)} \tag{6}$$

where B is Bulk Modulus,

G is the hear Modulus,

Y is Young Modulus,

v is the Poisson's ratio.

The ability to resist the deformation and flexibility of the gemstone is represented by the equation

$$H = \frac{1 - 2v}{6(1 + v)} Y \tag{7}$$

where H is the hardness or stiffness constant,

v is Poisson's ratio,

Y is the Young's modulus.

3. Results and Discussion

The optimized structure was subjected to force fields, with an ultra-fine quality setting of 2×10^{-5} kcal/mol of energy, 0.001 kcal/mol/Å of force, and 1×10^{-5} Å of displacement in order to investigate its stability conditions. Figure 3 represents the optimized structure, and all the constituent atoms of the aquamarine gemstone with their respective positions.

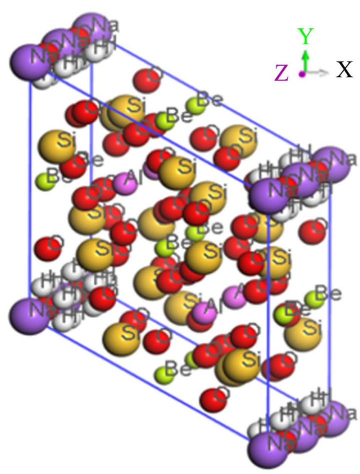

Figure 3. The optimized structure.

The crystal lattice parameters $a = b = 9.2909$ Å; $c = 9.1996$ Å; $\alpha = 90$; $\beta = 90$; $\gamma = 270$; $V = 687.726$ Å^3 which is concurrent with the results reported in the crystalline database with Be, Al Si, and O [2].

The Born stability conditions are represented by **Figure 4**, whereby C_{11} indicates the stiffness of the material (**Figure 4(a)**), C_{12} shear stress (**Figure 4(b)**), and C_{44} shear deformation (**Figure 4(c)**). **Figure 4(a)** indicates the values of stiffness oscillate with variations of external pressure, this indicates that aquamarine gemstones are stable against strain. While shear stress values oscillated in positive and negative values (**Figure 4(b)**), the positive values outperformed the negative values. This also shows that the gemstone considered in this study is strongly against shear stress. However, C_{11} is 0 GPa at the external pressure 140 GPa and C_{12} is 4800 GPa at that particular pressure, this violate the stiffness condition one from equation 2 mean while at C_{11} is less 1400 Gpa while C_{12} is 2400 Gpa at the external pressure 60 GPa which also violet the Born stiffness condition. **Figure 4(c)**, large portions of shear deformation to the negative side, this indicates that aquamarine gemstone to a large extent opposes the shear deformation [25]. With these parameters considered for Born stability, we can conclusively say that aquamarine gemstone is has accepted Born stability conditions except at external pressure 60 GPa and 140 GPa.

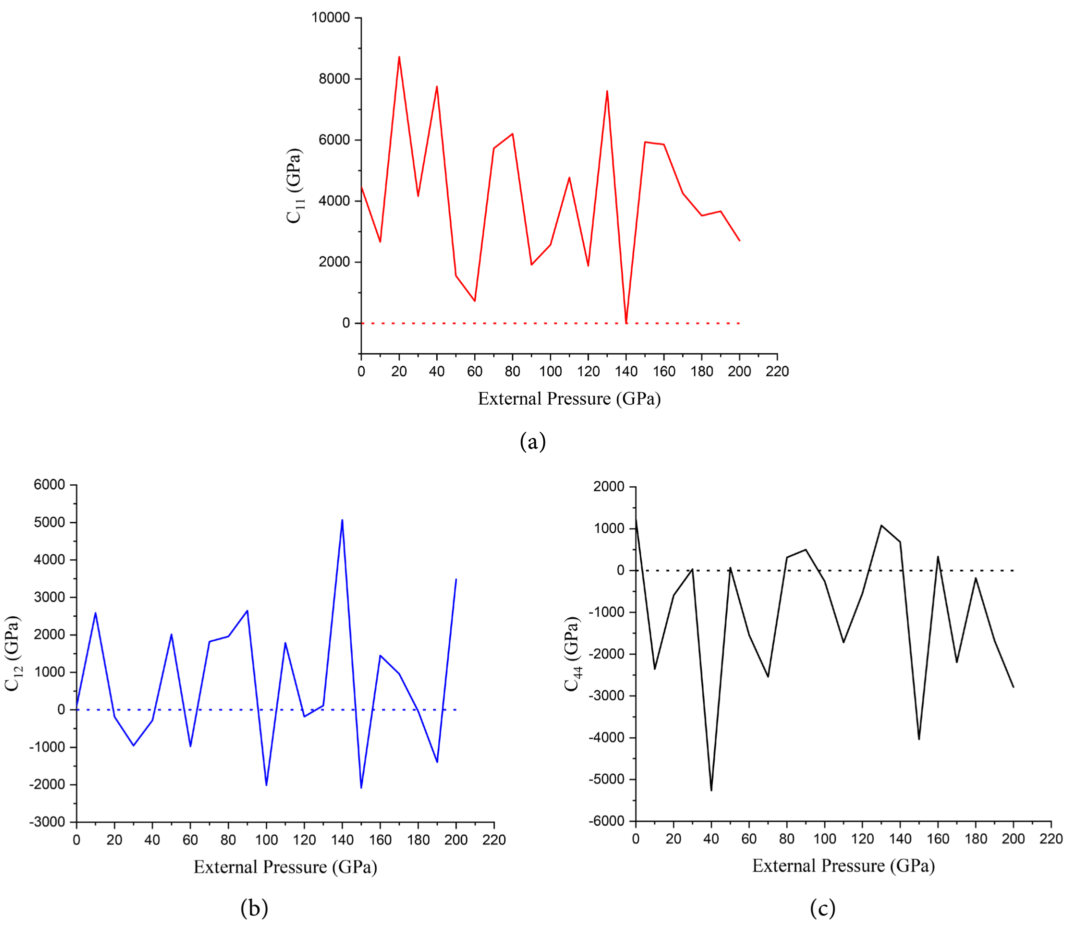

Figure 4. (a) C_{11} vs external pressure, (b) C_{12} vs external pressure (GPa), (c) C_{44} vs external pressure (GPa).

On the basis of mechanical properties such as compressibility, bulk modulus, and shear modulus with variations of external pressure were also investigated. Figures 5-7 present the fluctuations of compressibility, bulk modulus and shear modulus with external pressure respectively. As it can be seen from all three curves, the beryllium aluminum silicate material is mechanically stable at the external pressure 0 - 40 GPa and above 120 GPa. This stability is indicated by small oscillations, while it was unstable at the pressure of around 50 - 120 GPa.

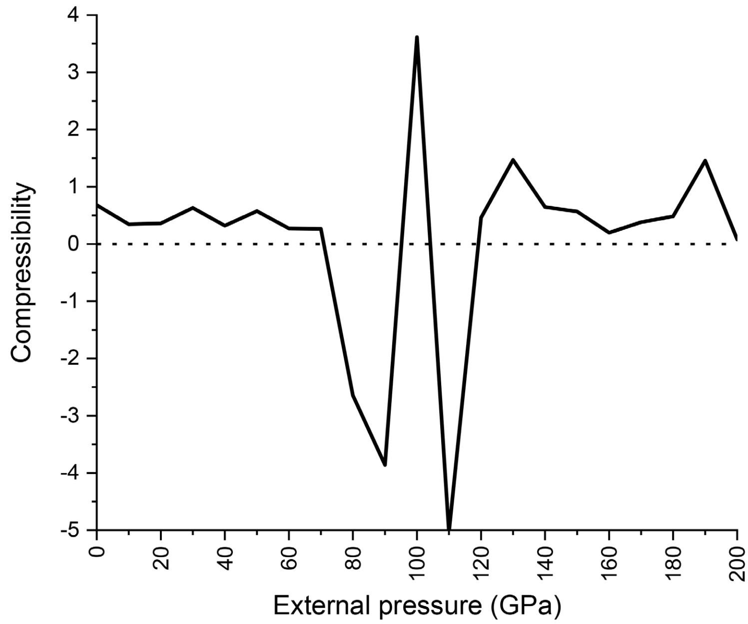

Figure 5. Compressibility vs external pressure.

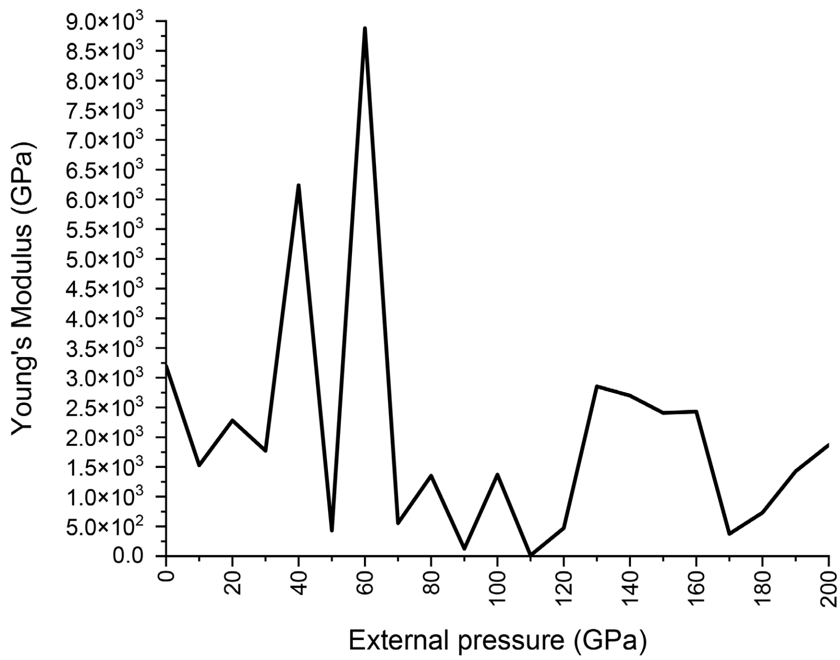

Figure 6. Young's modulus with external pressure.

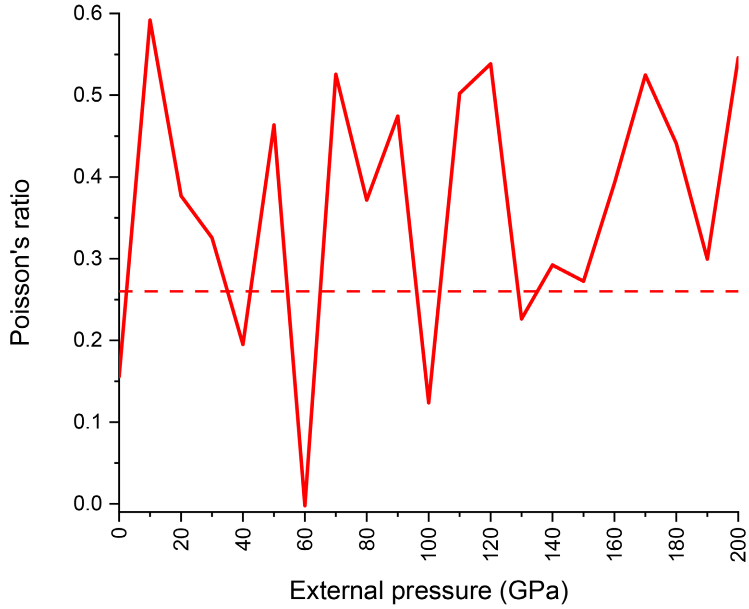

Figure 7. Poisson's ratio with external pressure.

Other important parameters for determining the hardness of the crystalline material are Young's modulus, Poisson's ratio (v) and Young's modulus tells how the material can withstand once subjected to elastic deformation. **Figure 6** shows the variations of the young modulus with the applied external pressure. In the range where the beryllium aluminum silicate material was found to be mechanically stable, the values of Young's modulus varied from 0 - 9000 GPa. Thus, this material is mechanically stable within that range of external pressure. While the average value of Poisson's ratio was 0.26 as indicated in **Figure 7**, this value is within other crystalline materials found in the literature [8] [16] [28].

The critical value of Poisson's ratio is 0.28 [29], where changes from brittle materials to ductile materials. The materials are regarded as ductile materials when $0.2857 < v \ll 0.5$ and as brittle materials $0.125 < v < 0.285$ [30]. Moreover, some materials have both ductile and brittle properties, and their Poisson ratio range varies from 0.26 to 0.42 [29] [30]. Therefore, it is seen from **Figure 7** that most values of the Poisson ratio with increasing external pressure dominated above the average value of 0.26. Hence, aquamarine gemstone considered in this study exhibits ductile properties.

4. Conclusion

Aquamarine gemstone (beryllium aluminium silicate) with chemical formula $Be_3Al_2Si_6O_{18}$ which crystallizes in the hexagonal system with P6/mcc (192) space group its effect of external pressure on mechanical properties has been studied using the First principle. Using Materials Studio simulation, the forcite module was used to calculate mechanical properties at convergence tolerance energy of 2e−005 kcal/mol, the force of 0.001 kcal/mol/A, and tress of 0.001 GPa while applying the external pressure within the range of 0 - 200 GPa on the optimized structure at electrostatic and Van der Waals terms Ewald. The results show that the independent elastic constants are mechanically stable at 0 GPa to 40 GPa, above 120 Gpa, and unstable at 60 - 120 Gpa. While the average bulk modulus, shear modulus, Young's modulus, and Poisson's ratio are 2319.9447, 652.3058, 1789.2236, and 0.26 respectively. The compressibility of the material was found to be 0.059921/TPa, this indicates that aquamarine gemstones are stable against strain and strongly against shear stress but opposing shear deformation. These values are within other crystalline materials found in the literature [28]-[30]. Furthermore, this provides technological backing for the comprehensive valuation of mechanical properties, quality, and stability of gemstones available in Tanzania.

Acknowledgements

The Tanzania Atomic Energy Commission as a government institution has funded the research described in this publication. The sponsors' views are not reflected in the opinions, results, conclusions, or suggestions made in this work; rather, they are the authors' alone.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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